Acknowledgment.—The authors wish to thank Mr. O. P. Crews and his staff for the preparation of large amounts of certain of the intermediates. They also wish to thank Dr. Peter Lim's group for the ultraviolet and infrared spectra, the paper chromatography, and the optical rotations.

The Preparation of 2(5H)-Furanones and Dyes Derived from Them

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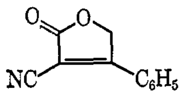
Alkali metal salts of acetic acids substituted with one electron-withdrawing group react with α-halocarbonyl compounds to give α-oxoalkyl esters which cyclize to 2(5H)-furanones. The acidic C_5-methylene groups in these furanones may be used to form hydrazones, azomethines, and a variety of polymethine dyes.

A recent review article has summarized the known methods of making 2(5H)-furanones.[1] We report here a new method involving the reaction of α-halo ketones with alkali metal salts of acetic acids substituted with one electron-withdrawing group. For example, sodium cyanoacetate and 2-bromoacetophenone were condensed to give 3-cyano-4-phenyl-2(5H)-furanone (**1**). Data



1

for **1** and other 2(5H)-furanones made by this procedure are given in Table I.

Table I

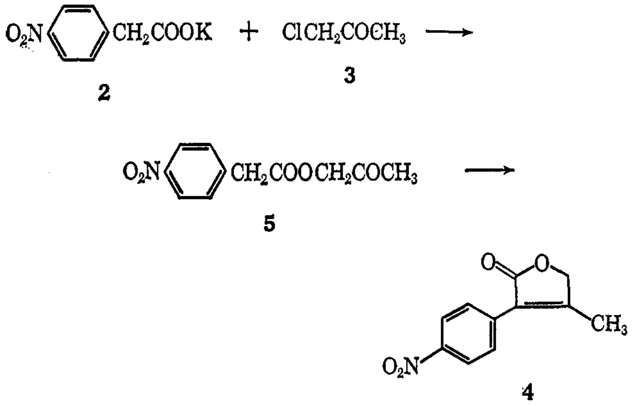
2(5H)-Furanones

Compound	% yield	Recrystn solvent	Mp, °C	Analyses
3-Cyano-4-phenyl-2(5H)-furanone (**1**)	39.4	Acetonitrile	164–167	Calcd for $C_{11}H_7NO_2$: C, 71.3; H, 3.79; N, 7.5. Found: C, 70.9; H, 3.4; N, 7.4.
4-*p*-Bromophenyl-3-cyano-2(5H)-furanone	32.1	Acetonitrile	215–218	Calcd for $C_{11}H_6BrNO_2$: C, 50.0; H, 2.27; Br, 30.3. Found: C, 49.9; H, 2.2; Br, 30.1.
4-*p*-Bromophenyl-3-*p*-nitrophenyl-2(5H)-furanone	19.2	DMF	214.5–216	Calcd for $C_{16}H_{10}BrNO_4$: C, 53.4; H, 2.78; Br, 22.2; N, 3.89. Found: C, 53.1; H, 2.6; Br, 22.4; N, 4.0.
3,4-Di-*p*-nitrophenyl-2(5H)-furanone	46.6	Acetonitrile	207–208.5	Calcd for $C_{16}H_{10}N_2O_6$: C, 58.9; H, 3.07; N, 8.59. Found: C, 59.0; H, 3.0; N, 8.9.
4-Methyl-3-*p*-nitrophenyl-2(5H)-furanone (**4**)	34.0	Acetic acid	142–144	Calcd for $C_{11}H_9NO_4$: C, 60.3; H, 4.11; N, 6.38. Found: C, 59.9; H, 4.1; N, 6.1.

The structure of **1** was established by instrumental evidence and by a two-step conversion in low yield to the known[2] 3-carbamoyl-4-phenylmaleic anhydride.

The reaction path for this 2(5H)-furanone synthesis involves initial formation of the α-oxoalkyl ester and then cyclodehydration. Treatment of potassium *p*-nitrophenylacetate (**2**) with chloroacetone (**3**) for 20 hr in boiling methanol gave 4-methyl-3-*p*-nitrophenyl-2(5H)-furanone (**4**) and a small amount of acetonyl *p*-nitrophenylacetate (**5**). When **2** and **3** were stirred for 24 hr in methanol at room temperature, only **5** was isolated. Boiling **2** and **3** for 72 hr in methanol gave **4**, methyl *p*-nitrophenylacetate, and no **5**. The cyclization of **5** to **4** was accomplished by boiling **5** for 1 hr in methanol containing a trace of **2**.

A limitation on the scope of this method is that the electron-withdrawing group on the acetic acid must be strong in order for cyclization of the α-oxoalkyl ester to occur. For example, the treatment of 2,4′-dibromoacetophenone with **2** gave 4-*p*-bromophenyl-3-*p*-nitrophenyl-2(5H)-furanone, but sodium phenylacetate gave *p*-bromophenacyl phenylacetate. Efforts to cyclize this ester by using concentrated sulfuric acid, potassium *t*-butoxide, polyphosphoric acid, and ammonium acetate–acetic acid were unsuccessful.



The reactivity of the methylene group in 2(5H)-furanones obtainable by this procedure makes them useful dye intermediates. For instance, **1** coupled with benzenediazonium chloride to give 4-cyano-3-phenyl-2,5-dihydrofuran-2,5-dione-2-phenylhydrazone (**5**) (Chart I), with N,N-dimethyl-*p*-nitrosoaniline to give the azomethine, 3-cyano-5-*p*-dimethylaminophenylimino-4-phenyl-2(5H)-furanone (**7**), with Fischer's aldehyde (2-methylene-1,3,3-trimethylindoline-ω-carboxaldehyde) to give the merocyanine, 3-cyano-4-phenyl-5-[2-(1,3,3-trimethylindolin-2-ylidene)ethylidene]-2(5H)-

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[1] Y. S. Rao, *Chem. Rev.*, **64**, 360 (1964).

[2] Z. Jerzmanowska and M. Jaworska-Krôlikowska, *Roczniki Chem.*, **28**, 397 (1954); *Chem. Abstr.*, **50**, 288 (1956).

TABLE II

DYES FROM 2(5H)-FURANONES

Compound	% yield[a]	Recrystn solvent	Mp, °C	λ_{max}	Log ϵ	Analyses
4-Cyano-3-phenyl-2,5-dihydrofuran-2,5-dione-2-phenylhydrazone (**6**)	22	*n*-Butyl alcohol	256–258	334 (dioxane) 463 (dioxane)	3.99 4.42	Calcd for $C_{17}H_{11}N_3O_2$: C, 70.5; H, 3.81; N, 14.5. Found: C, 70.8; H, 3.9; N, 14.4.
4-Cyano-3-phenyl-2,5-dihydrofuran-2,5-dione-2-*p*-N-ethyl-N-2-hydroxyethylaminophenylhydrazone	17.7	Tetrahydrofuran–acetonitrile	195–196	273 (THF) 312 (THF) 350 (THF) 602 (THF)	4.08 4.08 3.99 4.08	Calcd for $C_{21}H_{20}N_4O_3$: C, 67.0; H, 5.32; N, 14.9. Found: C, 67.1; H, 5.3; N, 15.0.
3-Cyano-5-*p*-dimethylaminophenylimino-4-phenyl-2(5H)-furanone (**7**)	51.6	Dioxane	247–248	242 (THF) 273 (THF) 552 (THF)	4.30 4.26 4.45	Calcd for $C_{19}H_{15}N_3O_2$: C, 71.8; H, 4.73; N, 13.3. Found: C, 71.4; H, 4.6; N, 13.4.
5-*p*-Dimethylaminophenylimino-3,4-di-*p*-nitrophenyl-2(5H)-furanone	5.1	Ethyl acetate	220–221	273 (dichloroethane) 520 (dichloroethane)	4.66 2.49	Calcd for $C_{24}H_{18}N_4O_6$: C, 62.9; H, 3.96; N, 12.2. Found: C, 62.4; H, 4.0; N, 12.0.
3-Cyano-4-phenyl-5-[2-(1,3,3-trimethylindolin-2-ylidene)ethylidene]-2(5H)-furanone (**8**)	9.2	Pyridine	279–281	555 (methanol)	5.01	Calcd for $C_{24}H_{20}N_2O_2$: C, 78.3 H, 5.43; N, 7.61. Found: C, 77.9; H, 5.5; N, 7.6.
Bis[3-cyano-4-phenyl-2(5H)-furanone-(5)]-monomethinoxonol, pyridine salt (**9**)	32.8	Pyridine	276–277	298 (DMF) 373 (DMF) 605 (DMF)	4.08 3.96 5.06	Calcd for $C_{28}H_{18}N_3O_4$: C, 73.0; H, 3.91; N, 9.13. Found: C, 72.8; H, 3.6; N, 9.1.
Bis[3-cyano-4-phenyl-2(5H)-furanone-(5)]-trimethinoxonol, triethylamine salt (**10**)	36.2	2-Butanone	220–221	282 (DMF) 303 (DMF) 318 (DMF) 363 (DMF) 412 (DMF) 444 (DMF) 523 (DMF) 716 (DMF)	3.90 3.91 3.90 3.76 3.48 3.48 3.78 5.08	Calcd for $C_{31}H_{29}N_3O_4$: C, 73.4; H, 5.72; N, 8.28. Found: C, 73.8; H, 6.0; N, 8.5.
5-Benzylidene-3-cyano-4-phenyl-2(5H)-furanone (**11**)	82.3	Toluene	203–205	373 (DMF)	4.00	Calcd for $C_{18}H_{10}NO_2$: C, 79.2; H, 4.03; N, 5.13. Found: C, 79.1; H, 3.8; N, 5.2.
3-Cyano-5-*p*-dimethylaminobenzylidene-4-phenyl-2(5H)-furanone	79.0	Chlorobenzene	235–237	277 (DMF) 534 (DMF)	3.88 3.71	Calcd for $C_{20}H_{16}N_2O_2$: C, 76.0; H, 5.06; N, 8.87. Found: C, 75.7; H, 5.2; N, 8.8
5,5′-Terephthalylidenebis[3-cyano-4-phenyl-2(5H)-furanone]	95.8	*b*	393–396[c]	442 (DMF)	4.78	Calcd for $C_{30}H_{16}N_2O_4$: C, 76.8; H, 3.42; N, 5.96. Found: C, 76.6; H, 3.6; N, 5.8.
3-Cyano-5-*p*-dimethylaminocinnamylidene-4-phenyl-2(5H)-furanone	34.0	Toluene	169–171	289 (THF) 322 (THF) 528 (THF)	4.08 4.08 4.38	Calcd for $C_{24}H_{20}N_2O_2$: C, 77.2; H, 5.24; N, 8.18. Found: C, 76.8; H, 5.2; N, 8.2.
3-Cyano-5-(2,5-dihydroxybenzylidene)-4-phenyl-2(5H)-furanone	31.3	Tetrahydrofuran	312–314	320 (DMF) 488 (DMF)	4.00 4.08	Calcd for $C_{18}H_{11}NO_4$: C, 70.8; H, 3.61; N, 4.58. Found: C, 71.1; H, 3.6; N, 4.5.

furanone (**8**), with triethyl orthoformate in pyridine solution to give the pyridine salt of bis[3-cyano-4-phenyl-2(5H)-furanone-(5)]monomethinoxonol (**9**), and with 1,3,3-trimethoxypropene in pyridine containing triethylamine to give the corresponding trimethinoxonol (**10**) as the triethylamine salt.

The reaction of **1** with benzaldehyde in boiling toluene containing a trace of piperidine acetate was rapid and gave 5-benzylidene-3-cyano-4-phenyl-2(5H)-furanone (**11**). Under these conditions, **1** reacted more slowly with cyclohexanone and failed to react with acetophenone. The desired dye from acetophenone, 3-cyano-5-α-methylbenzylidene-4-phenyl-2(5H)-furanone (**12**), was obtained by heating **1** with acetophenone diethyl ketal. The furanone **4**, in which both the C_5-methylene group and the methyl on C_4 are conjugated with the *p*-nitrophenyl and the lactone carbonyl, when treated with 2 equiv of benzaldehyde, gave only a monobenzylidene compound. The nmr spectrum showed that condensation had occurred at C_5 to give 5-benzylidene-4-methyl-3-*p*-nitrophenyl-2(5H)-furanone.

The reaction of **1** (Scheme I) with phosphoryl chloride in N,N-dimethylformamide gave 3-cyano-5-dimethylaminomethylene-4-phenyl-2(5H)-furanone (**13**). The identity of **13** was confirmed by hydrolysis to dimethylamine hydrochloride and 3-cyano-5-hydroxymethylene-4-phenyl-2(5H)-furanone which, upon treatment with **1**, gave **9**. Further confirmation came from reaction of **13** with 3-ethyl-2-methylbenzothiazolium iodide to give the merocyanine, 3-cyano-5-[3-ethyl-2-benzothiazolylideneethylidene]-4-phenyl-2-(5H)-furanone (**14**), which was identical with a sample of **14** made by the reaction of **1** with 2-β-acetanilidovinyl-3-ethylbenzothiazolium iodide.[3]

The reaction of **13** with malononitrile gave 3-cyano-5-(2-dicyanoethylidene)-4-phenyl-2(5H)-furanone (**15**) (Chart II) as the triethylamine salt. The unsymmetrical oxonol **16** came from reaction of **13** with 3,4-di-*p*-nitrophenyl-2(5H)-furanone and the merophospho-

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[3] The authors are grateful to Mr. John Mee, of these laboratories, for providing the physical constants of **14** which he synthesized by the latter route.

TABLE II

(*Continued*)

Compound	% yield[a]	Recrystn solvent	Mp, °C	λ_{max}	Log ϵ	Analyses
5-Benzylidene-4-methyl-3-*p*-nitrophenyl-2(5H)-furanone	83.3	Chlorobenzene	229–231	366 (DMF)	4.57	Calcd for $C_{18}H_{13}NO_4$: C, 70.3; H, 4.23; N, 4.56. Found: C, 70.6; H, 4.5; N, 4.5.
5-Cinnamylidene-3-cyano-4-phenyl-2(5H)-furanone	29.4	Chlorobenzene	243–244	270 (DMF) 422 (DMF)	3.94 4.56	Calcd for $C_{20}H_{13}NO_2$: C, 80.2; H, 4.35; N, 4.68. Found: C, 80.4; H, 4.4; N, 4.7.
3-Cyano-5-[9-(1H,5H-benzo[*ij*]quinolizine)-methylene]-4-phenyl-2(5H)-furanone	67.6	Chlorobenzene	254 dec	315 (DMF) 578 (DMF)	4.02 4.77	Calcd for $C_{24}H_{20}N_2O_2$: C, 78.3; H, 5.44; N, 7.61. Found: C, 77.9; H, 5.7; N, 7.3.
5-*p*-Dimethylaminobenzylidene-3,4-di-*p*-nitrophenyl-2(5H)-furanone	86.7	Dioxane	322–323	262 (dichloroethane) 520 (dichloroethane)	3.96 4.23	Calcd for $C_{25}H_{19}N_3O_6$: C, 65.6; H, 4.19; N, 9.19. Found: C, 65.8; H, 4.4; N, 9.0.
5-[4,4′-Bis(dimethylaminophenyl)methylene]-3-cyano-4-phenyl-2(5H)-furanone	47.8	Chlorobenzene	258–260[d]	283 (THF) 546 (THF)	4.28 4.46	Calcd for $C_{28}H_{25}N_3O_2$: C, 77.2; H, 5.75; N, 9.66. Found: C, 77.2; H, 5.6; N, 9.6.
3-Cyano-5-cyclohexylidene-4-phenyl-2(5H)-furanone	45.3	Ethanol	130–133	323 (THF)	4.37	Calcd for $C_{17}H_{15}NO_2$: C, 77.0; H, 5.66; N, 5.28. Found: C, 76.8; H, 5.6; N, 5.1.
3-Cyano-5-α-methylbenzylidene-4-phenyl-2(5H)-furanone (**12**)	9.8	Ethanol	171–173	331 (dichloroethane)	4.28	Calcd for $C_{19}H_{13}NO_2$: C, 79.4; H, 4.56; N, 4.88. Found: C, 79.1; H, 4.8; N, 4.8.
3-Cyano-5-dimethylaminomethylene-4-phenyl-2(5H)-furanone (**13**)	96.4	Acetonitrile	221–223	403 (DMF)	4.65	Calcd for $C_{14}H_{12}N_2O_2$: C, 70.0; H, 5.0; N, 11.7. Found: C, 69.7; H, 5.3; N, 11.6.
3-Cyano-5-[3-ethyl-2-benzothiazolylidene-ethylidene]-4-phenyl-2(5H)-furanone (**14**)	58	Pyridine	279–281	570 (5% pyridine in methanol)	5.14	Calcd for $C_{22}H_{16}N_2O_2S$: C, 70.9; H, 4.30; N, 7.52; S, 8.60. Found: C, 70.8; H, 4.3; N, 7.5; S, 8.7.
3-Cyano-5-formyl-4-phenyl-2(5H)-furanone 2,4-dinitrophenylhydrazone	50	Acetonitrile	212–214	361 (THF)	4.38	Calcd for $C_{18}H_{11}N_5O_6$: C, 55.0; H, 2.80; N, 17.8. Found: C, 54.7; H, 3.1; N, 17.5.
3-Cyano-5-(2-dicyanoethylidene)-4-phenyl-2(5H)-furanone, triethylamine salt	50.8	Ethyl acetate	149–151	470 (THF)	4.76	Calcd for $C_{21}H_{22}N_4O_2$: C, 69.6; H, 6.08; N, 15.5. Found: C, 69.4; H, 6.1; N, 15.5.
[3-Cyano-4-phenyl-2(5H)-furanone-(5)] [3,4-di-*p*-nitrophenyl-2(5H)-furanone-(5)]-monomethinoxonol, triethylamine salt (**16**)	43	Pyridine	275–276	387 (DMF) 666 (DMF)	3.75 4.86	Calcd for $C_{34}H_{31}N_4O_8$: C, 65.5; H, 4.97; N, 8.99. Found: C, 65.6; H, 4.9; N, 8.8.
2-(3-Cyano-2,5-dihydro-2-oxo-4-phenyl-5-furylidenemethyl)cyclopentadienylidenetriphenylphosphorane (**17**)	69.1	Chlorobenzene	241–242	536 (THF)	4.91	Calcd for $C_{35}H_{24}NO_2P$: C, 80.6; H, 4.60; N, 2.69; P, 5.95. Found: C, 80.9· H, 5.0; N, 2.5; P, 5.9.

[a] Recrystallizations were repeated until a constant melting point was obtained; % yields are those for material purified in this way. [b] Slurried in boiling DMF. [c] Determined on Mel-Temp apparatus, Laboratory Devices, Cambridge, Mass. [d] Sintered at 233°.

cyanine **17** from reaction with cyclopentadienylidenetriphenylphosphorane.

Data for the dyes made from these 2(5H)-furanones are found in Table II.

Experimental Section[4,5]

3-Cyano-4-phenyl-2(5H)-furanone (1).—A solution of 170 g (2.00 moles) of cyanoacetic acid, 80.0 g (2.00 moles) of sodium hydroxide, 3 l. of ethanol, 720 ml of water, and 398 g (2.00 moles) of 2-bromoacetophenone was refluxed, with stirring, for 1 hr. The solid which separated upon cooling to room temperature was recrystallized from 800 ml of acetonitrile to give 145.9 g (39.4%) of straw-colored crystals: mp 164–167°, λ_{CN}^{KBr} 4.45 μ, λ_{C-O}^{KBr} 5.72 μ, nmr spectrum (dimethyl sulfoxide) 5.71 (singlet, 2) and 7.83 (multiplet, 5). The mass spectrum gave a parent peak of 185 mass units.

4-Methyl-3-*p*-nitrophenyl-2(5H)-furanone (4). A.—A solution of 36.2 g (0.200 mole) of *p*-nitrophenylacetic acid, 11.2 g (0.200 mole) of potassium hydroxide, 0.5 g of sodium iodide, 18.6 g (0.200 mole) of chloroacetone, and 250 ml of methanol was refluxed, with stirring, for 20 hr. Cooling in ice caused a solid to separate which was slurried in water and recrystallized from glacial acetic acid to give 14.9 g (34.0%) of pale yellow crystalline **4**, mp 143–145°.

Dilution of the methanol filtrate with water and recrystallization of the separated solid from methanol gave 3.1 g (6.5%) of **5**, mp 86–88°.

Anal. Calcd for $C_{11}H_{11}NO_5$: C, 55.6; H, 4.64; N, 5.90. Found: C, 55.5; H, 4.6; N, 6.0.

Stirring 2.5 times the quantities in A at room temperature for 24 hr, dilution with water, cooling in ice, and recrystallization of the separated solid from carbon tetrachloride gave 6.0 g (5.1%) of **5**, mp 85.5–87.5°.

Increasing the reaction time in A to 72 hr gave a 26.4% yield of **4**. Dilution of the filtrate with water and recrystallization of

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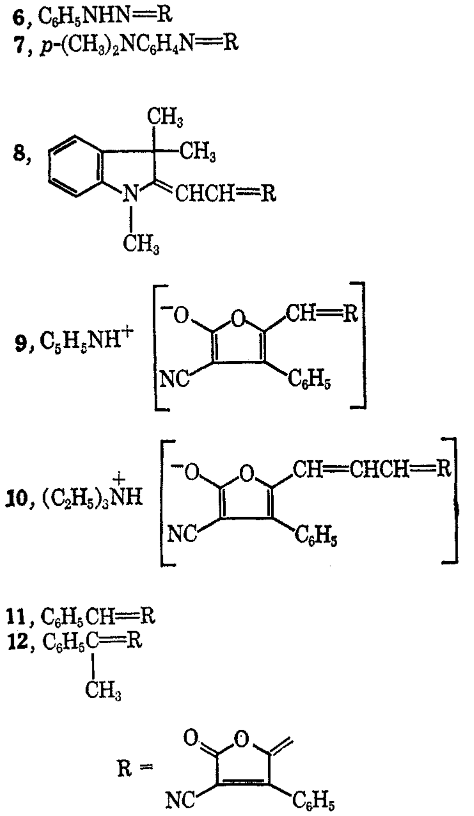
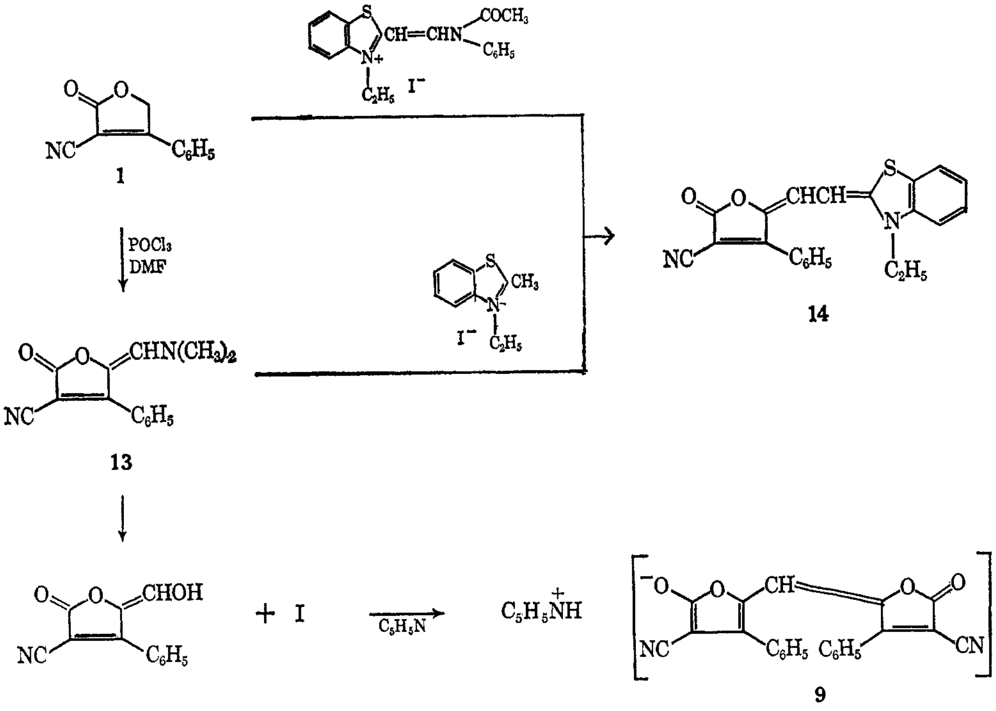
(4) Melting points were determined in a Thomas-Hoover, capillary melting point apparatus, unless otherwise noted, and are corrected. Infrared spectra were determined as potassium bromide pressings on a Baird double-beam spectrophotometer, Model NK-1, and sodium chloride optics, mass spectra on a 60° sector-type mass spectrometer built in these laboratories, with an all-glass, heated inlet system operated at 235°, and nmr spectra on a Varian Model A-60 spectrometer, peak positions being reported in parts per million relative to internal tetramethylsilane.

(5) When several of the same class of compounds in Tables I and II were produced by the same method, only one representative procedure is presented.

CHART I



SCHEME I



the filtered solid from methanol gave an 8.4% yield of methyl p-nitrophenylacetate, mp 53–54° (lit. mp 54°).[6]

Anal. Calcd for $C_9H_9NO_4$: C, 55.4; H, 4.62; N, 7.19. Found: C, 55.3; H, 4.7; N, 7.2.

B. A solution of 2.0 g (0.0084 mole) of **5**, 0.2 g of p-nitrophenylacetic acid, 2 drops of 10% potassium hydroxide, and 30 ml of methanol was refluxed for 1 hr and allowed to stand for 24 hr to give 1.4 g (65%) of **5**, mp 143–145°.

4-Cyano-3-phenyl-2,5-dihydrofuran-2,5-dione-2-phenylhydrazone (6).—Dropwise addition, with stirring, at 0–5° of a solution of benzenediazonium chloride from 6.9 g (0.10 mole) of sodium nitrite, 9.3 g (0.10 mole) of aniline, 50 ml of 6 *N* hydrochloric acid, and 30 ml of water to a solution of 18.5 g (0.100 mole) of **1**, 500 ml of acetone, and 24 g of aqueous 28% ammonia, followed by stirring for an additional 0.5 hr, caused the separation of a solid which was recrystallized from 800 ml of n-butyl alcohol to give 6.3 g (22%) of rust red needles: mp 256–257.5°, λ_{NH}^{KBr} 3.12 μ, λ_{CN}^{KBr} 4.48 μ, $\lambda_{C=O}^{KBr}$ 5.70 μ, nmr spectrum (dimethyl sulfoxide) 7.73 (multiplet) and 11.8 (singlet, exchangeable with deuterium oxide).

3-Carbamoyl-4-phenylmaleic Anhydride.—A mixture of 5.7 g (0.020 mole) of **6** and 50 ml of concentrated sulfuric acid was stirred for 24 hr and then poured onto 400 g of crushed ice. The orange, filtered solution was extracted with chloroform. The combined extracts were washed with water. Two recrystallizations from chloroform of the residue from concentration of the extracts gave 0.08 g (2%) of pale yellow crystals, mp 158–159° (lit. mp 157–158°).[2]

Anal. Calcd for $C_{11}H_7NO_4$: C, 60.8; H, 3.22; N, 6.45. Found: C, 60.6; H, 3.1; N, 6.6.

3-Cyano-5-p-dimethylaminophenylimino-4-phenyl-2(5H)-furanone (7).—Refluxing a mixture of 37.0 g (0.200 mole) of **1**, 30.0 g (0.200 mole) of N,N-dimethyl-p-nitrosoaniline, and 400 ml of dioxane for 1 hr and allowing it to cool overnight to room temperature gave 32.7 g (51.6%) of shiny green crystals, mp 247–248°.

5-Benzylidene-3-cyano-4-phenyl-2(5H)-furanone (11).—A mixture of 10.0 g (0.0539 mole) of **1**, 5.7 g (0.054 mole) of benzaldehyde, 0.5 ml of piperidine, 0.5 ml of glacial acetic acid, and 150 ml of toluene was refluxed for 0.5 hr, during which time 1 ml of water was removed azeotropically. Cooling in ice and recrystallization of the separated solid from 150 ml of toluene gave 12.1 g (82.3%) of yellow crystals, mp 203–205°.

3-Cyano-5-cyclohexylidene-4-phenyl-2(5H)-furanone.—Cyclohexanone and **1** were allowed to react by the procedure used to make **11**, except that the reaction time was 3 hr and 0.5-ml portions of piperidine and acetic acid were added every 0.5 hr. Concentration at the water pump, followed by two recrystallizations of the residue from isopropyl alcohol, gave 24.0 g (45.3%) of colorless crystals, mp 130–133°.

5-[4,4'-Bis(dimethylaminophenyl)methylene]-3-cyano-4-phenyl-2(5H)-furanone.—A mixture of 34.2 g (0.100 mole) of di-(4-dimethylaminophenyl)diethoxymethane, 18.5 g (0.100 mole) of **1**, and 400 ml of xylene was distilled, with slow mechanical stirring, through a 6-in. glass column packed with 0.25-in. glass helices. During 1 hr the column temperature rose from 76 to 125°. The solid which separated upon cooling overnight to room temperature was filtered and recrystallized twice from

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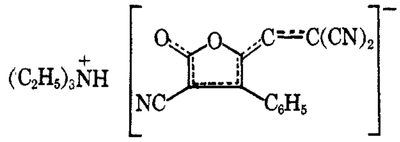
(6) T. Maxwell, *Ber.*, **12**, 1765 (1879).

CHART II



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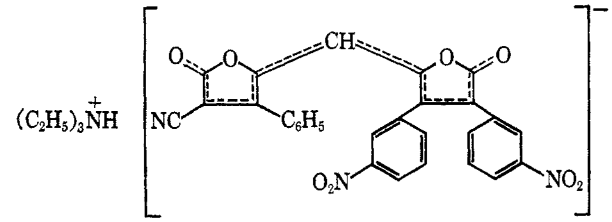

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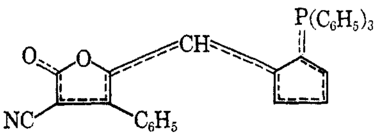

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chlorobenzene to give 20.8 g (47.8%) of green crystals, mp 258–261°, with sintering at 234°.

Bis[3-cyano-4-phenyl-2(5H)-furanone-(5)]monomethinoxonol, Pyridine Salt (9). A.—A mixture of 37.0 g (0.200 mole) of **1**, 14.8 g (0.100 mole) of triethyl orthoformate, and 250 ml of pyridine was refluxed for 1 hr and then cooled in an ice bath. The separated solid was recrystallized from 300 ml of pyridine to give 15.1 g (32.8%) of green crystals, mp 276–277°.

B.—Refluxing a mixture of 12.0 g (0.0652 mole) of **1**, 13.9 g (0.0652 mole) of 3-cyano-5-hydroxymethylene-4-phenyl-2(5H)-furanone, and 150 ml of pyridine for 3 hr, cooling, collection of the solid, and recrystallization from pyridine gave 8.4 g (28%) of **9**, mp 275–276°.

[3-Cyano-4-phenyl-2(5H)-furanone-(5)]-[3,4-di-*p*-nitrophenyl-2(5H)-furanone-(5)]monomethinoxonol, Triethylamine Salt (16).—Reaction of equimolar amounts of 3,4-di-*p*-nitrophenyl-2(5H)-furanone, triethylamine, and **13** in pyridine according to procedure B used to make **9** gave a 43% yield of shiny green crystals, mp 275–276°.

3-Cyano-5-dimethylaminomethylene-4-phenyl-2(5H)-furanone (13).—To 400 ml of dimethylformamide, there was added slowly (temperature being kept below 30°), with stirring and cooling, 61.2 g (0.400 mole) of phosphoryl chloride and then in one portion 74.0 g (0.400 mole) of **1**. The mixture was stirred for 2 hr (exotherm to 49°), cooled, and diluted with 300 ml of ice water. Collection of the solid and recrystallization from 900 ml of acetonitrile gave 83.2 g (86.6%) of yellow needles, mp 222–223°. The mass spectrum gave a parent peak of 240 mass units.

3-Cyano-5-hydroxymethylene-4-phenyl-2(5H)-furanone.—A mixture of 24.0 g (0.100 mole) of **13**, 300 ml of methanol, 4.0 g (0.10 mole) of sodium hydroxide, and 10 ml of distilled water was refluxed for 4 hr and then steam-distilled into a solution of 10 ml of concentrated hydrochloric acid and 100 ml of ethanol until the distillate was no longer basic. Evaporation of the distillate (800 ml) at room temperature and vacuum drying of the residue over anhydrous calcium sulfate gave 1.1 g of dimethylamine hydrochloride (mass spectrum identical with authentic sample). The cooled residue from the steam distillation was diluted with 500 ml of water and filtered. Acidification of the filtrate caused the separation of a solid which was washed with water and dried to give 20.2 g (94.7%): mp 218–221° (not raised by recrystallization from acetonitrile); λ_{OH}^{KBr} 3.22 μ; λ_{CN}^{KBr} 4.43 μ; $\lambda_{C=O}^{KBr}$ 5.75 μ; nmr spectrum (dimethyl sulfoxide) 7.36 (singlet, 1), 7.62 (singlet, 5), and 12.9 (singlet, 1) (exchangeable with deuterium oxide); 2,4-dinitrophenylhydrazone, yellow crystals from acetonitrile, mp 212–214°.

Anal. Calcd for $C_{12}H_7NO_3$: C, 67.6; H, 3.29; N, 6.57. Found: C, 67.4; H, 3.0; N, 6.5.

3-Cyano-5-[3-ethyl-2-benzothiazolylideneethylidene]-4-phenyl-2(5H)-furanone (14).—A stirred mixture of 12.7 g (0.0416 mole) of 3-ethyl-2-methylbenzothiazolium iodide, 10.0 g (0.0416 mole) of **13**, 1 ml of piperidine, and 200 ml of methanol was refluxed for 4 hr and allowed to cool overnight to room temperature. The separated solid was recrystallized twice from pyridine to give 8.9 g (58%) of shiny green crystals, mp 279–281°.

3-Cyano-5-(2-dicyanoethylidene)-4-phenyl-2(5H)-furanone, Triethylamine Salt (15).—A solution of 24.0 g (0.100 mole) of **13**, 6.6 g (0.10 mole) of malononitrile, 15 ml of triethylamine, and 150 ml of ethanol was refluxed for 3 hr and then cooled overnight in the refrigerator. The separated solid was recrystallized three times from ethyl acetate to give 18.4 g (50.8%) of orange-red crystals, mp 149–151°.

2-(3-Cyano-2,5-dihydro-2-oxo-4-phenyl-5-furylidenemethyl)-cyclopentadienylidenetriphenylphosphorane (17).—A stirred solution of 12.0 g (0.0500 mole) of **13**, 16.3 g (0.0500 mole) of cyclopentadienylidenetriphenylphosphorane, 1 ml of glacial acetic acid, and 200 ml of pyridine was refluxed for 1 hr, diluted with 200 ml of methanol, and cooled overnight in the refrigerator. Recrystallization of the separated solid from 100 ml of chlorobenzene gave 18.0 g (69.1%) of shiny gray crystals, mp 241–242°.

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A Total Synthesis of Phytol[1]

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A total synthesis of phytol from acetone is described. The synthesis has shorter stages than previously reported methods. Triethyl phosphonocrotonate anion could be condensed with carbonyl compounds to give the corresponding dienoic esters. The products were converted to β-keto sulfoxides by reaction with methylsulfinyl carbanion and the sulfoxides were reduced with aluminum amalgam to give methyl ketones. Phytone, one of the compounds prepared in this manner, was converted to phytol by two methods.

In an earlier paper[2] a six-step synthesis of isophytol from pseudoionone and propargyl alcohol was described. Recently, Nazarov,[3] Lukes,[4] and Maurit[5] succeeded in the total synthesis of phytol from laevulinic acid or acetylene; however, these syntheses are unfit for a large scale operation because of the number of steps involved.

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