TABLE I

PREPARATION OF FUROXANS

Furoxan	Dinitroölefins (Mol.)	Yield, %	B.p., °C. (Mm.)	n_D^{20}	Analysis Caled. C	Caled. H	Caled. N	Found C	Found H	Found N	Infrared Bands[6] γ Cm.$^{-1}$
3,4-Dimethyl[10]	trans-2,3-Dinitro-2-butene[5] (0.05)	75	60–62 (1.3)	1.4832	...	..	...	...	..	...	1616, 1165, 1041, 996, 850
3,4-Diethyl	3,4-Dinitro-3-hexene[12] (0.03)	70	66–67 (0.1)	1.4775	50.68	7.09	19.71	51.19	7.23	19.98	1600, 1142. 1037, 955, 843
3-Propyl-4-methyl	2,3-Dinitro-2-hexene[5] (0.04)	62	63–64 (0.15))	...	50.68	7.09	...	50.72	7.09	...	1600, 1150. 1015, 977, 847

(10) This infrared spectrum of this material was identical with that of authentic material (generously supplied by Dr. C. O. Parker) prepared by the action of dinitrogen tetroxide on dimethylglyoxime.[11]

(11) R. Scholl, *Ber.*, **23**, 3490 (1890).

(12) L. E. Bisgrove, J. F. Brown, and L. B. Clapp, *Org. Syntheses*, in press. We are indebted to Dr. Clapp for a preprint of this preparation.

mediate is generated and assumes the more stable, presumably the *trans* configuration.

EXPERIMENTAL[9]

Preparation of furoxans. Table I summarizes the data on the preparation of furoxans. All were prepared by exactly the same method which is outlined below for diphenylfuroxan.

Diphenylfuroxan. To a suspension of 2 g. (0.03 mole) of sodium azide in a mixture of 90 ml. of ethanol and 10 ml. of methanol was added a solution of 3 g. (0.01 mole) of *cis*-1,2-dinitrostilbene.[13] Gas evolution began immediately and heat was evolved. The solution gradually became orange as reaction continued. After the addition was completed, the mixture was heated under reflux for 1 hr., then poured into water and extracted with ether. After drying, the organic extracts were concentrated and the solid residue was recrystallized from ethanol to yield 2.3 g. (86%) of 3,4-diphenylfuroxan, m.p. 115–117° (lit.[14] m.p. 114–115°).

Reaction of sodium p-toluenethiolate with 3,4-Dinitro-3-hexene. A solution of 6.2 g. (0.05 mole) of *p*-toluenethiol in 50 ml. of absolute ethanol was added to a solution of 1.2 g. (0.05 g. atom) of sodium in 50 ml. of absolute ethanol. The resulting solution was cooled to 10–20° and 8.7 g. (0.05 mole) of either *cis* or *trans*-3,4-dinitro-3-hexene[5] in 25 ml. of ethanol was added slowly. An immediate precipitation of sodium nitrite occurred. The mixture was allowed to stand at room temperature for 30 min. It was then filtered, poured into water, and extracted with ether. The ether extracts were washed thoroughly with 10% sodium hydroxide solution, dried, and concentrated. There was obtained 10 g. (80%) of a yellow oil, whose infrared spectrum indicated it to be the desired nitroölefin derivative.

The oil was heated under reflux with 45 ml. of 30% hydrogen peroxide in 150 ml. of glacial acetic acid for 1 hr. The product, 3-*p*-toluenesulfonyl-4-nitro-3-hexene, was isolated in the usual manner and upon several recrystallizations from benzene-petroleum ether (30–60°) melted at 100–101.5°; yield 5 g. (55%).

Anal. Caled. for $C_{13}H_{17}NO_4S$: C, 55.10; H, 6.05; N, 4.94. Found: C, 55.02; H, 6.29; N, 4.77.

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(9) We are indebted to Dr. Keith S. McCallum for infrared interpretations.

(13) K. N. Campbell, J. S. Shavel, and B. K. Campbell, *J. Chem. Soc., Am.* **75**, 2400 (1953).

(14) E. Beckmann, *Ber.*, **22**, 1588 (1889).

Substituted Acrylonitriles from Heterocyclic Aldehydes and 3,4-Dimethoxyphenylacetonitrile

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In the course of studies in these laboratories a series of nine substituted acrylonitriles has been prepared by the condensation of heterocyclic aldehydes with 3,4-dimethoxyphenylacetonitrile. Two of these acrylonitriles (see Table I) have since been reported by Castle and Seese.[1] All of the compounds were screened as candidate hypotensive agents and were found to be inactive.

EXPERIMENTAL

The heterocyclic aldehydes used were all commercially available except julolidine-9-carboxaldehyde which was prepared by the method of Smith and Yu.[2]

α-3,4-Dimethoxyphenyl-β-(3-pyridyl)acrylonitrile. To a solution of 1.8 g. (0.01 mole) of 3,4-dimethoxyphenylacetonitrile and 1.1 g. (0.01 mole) of pyridine-3-aldehyde in 50 ml. of absolute ethanol was added 0.1 g. of potassium hydroxide. The solution was heated on the steam bath for 1 hr., then diluted with 25 ml. of water and chilled in an ice bath. The yellow crystals which appeared were filtered, washed with 15 ml. of 50% (vol.) ethanol, and recrystallized from 35 ml. of Methyl Cellosolve.

This procedure was followed in preparing the 2-quinolyl, 4-quinolyl, 3-isoquinolyl, 2-thienyl, and 2-furyl derivatives using the appropriate heterocyclic aldehyde. The 2-furyl derivative was recrystallized from 80% ethanol.

α-3,4-Dimethoxyphenyl-β-(4-pyridyl)acrylonitrile. A solution of 1.8 g. (0.01 mole) of 3,4-dimethoxyphenylacetonitrile and 1.1 g. (0.01 mole) of pyridine-4-aldehyde in 25 ml. of glacial acetic acid was saturated with anhydrous hydrogen chloride. The mixture was allowed to remain at room temperature for 2 days. It was then poured onto ice and the re-

(1) R. N. Castle and W. S. Seese, *J. Org. Chem.*, **20**, 987 (1955).

(2) P. A. S. Smith and T. Y. Yu, *J. Org. Chem.*, **17**, 1281 (1952).

TABLE I

SUBSTITUTED ACRYLONITRILES RCH=C(CN)–C$_6$H$_3$(OCH$_3$)–OCH$_3$

R	Formula	Yield, %[a]	M.P., °C.[b]	Color	Analyses: Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3-Pyridyl[c]	$C_{16}H_{14}N_2O_2$	69	142 -143.5	Light yellow	72.16	72.40	5.29	5.28
4-Pyridyl[d]	$C_{16}H_{14}N_2O_2$	18	141 -142	White	72.16	72.09	5.29	5.51
2-Quinolyl[e]	$C_{20}H_{16}N_2O_2$	63	139- 140	Light yellow	75.93	76.00	5.10	5.16
4-Quinolyl[f]	$C_{20}H_{16}N_2O_2$	41	180 -181.5	Yellow	75.93	75.85	5.10	5.29
3-Isoquinolyl[g]	$C_{20}H_{16}N_2O_2$	81	147 -148	Yellow	75.93	75.90	5.10	5.14
2-Furyl	$C_{15}H_{13}NO_3$	81	99 -100	Yellow-orange	70.57	70.57	5.13	5.24
3-Indolyl	$C_{19}H_{16}N_2O_2$	46	196 -197	Yellow	74.98	74.87	5.30	5.49
9-Julolidyl	$C_{23}H_{24}N_2O_2$	76	157.5-158.5	Yellow	76.64	76.60	6.71	6.84
2-Thienyl	$C_{15}H_{13}NO_2S$	91	122 -123.5	Yellow	66.41	66.37	4.83	4.68

[a] Yield of recrystallized product. [b] All melting points are uncorrected. [c] Literature m.p. 141–142° (Ref. 1). Hydrochloride salt, recrystallized from ethanol-water, yellow crystals, m.p. 220–222° dec. *Anal.* Calcd. for $C_{16}H_{14}N_2O_2$·HCl: C, 63.47; H, 4.99. Found: C, 63.68; H, 5.07. [d] Literature m.p. 138.5–139.5° (Ref. 1). [e] Hydrochloride salt, recrystallized from ethanol, red crystals, m.p. 229–231° dec. Anal. Calcd. for $C_{20}H_{16}N_2O_2$·HCl: C, 68.08; H, 4.86. Found: C, 68.27; H, 4.92. [f] Hydrochloride salt, recrystallized from ethanol-water, red crystals, m.p. 233–235° dec. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2$·HCl: C, 68.08; H, 4.86. Found: C, 67.83; H, 4.84. [g] Hydrochloride salt, recrystallized from ethanol, light green crystals, m.p. 105–107° dec. *Anal.* Calcd. for $C_{20}H_{16}N_2O_2$·HCl: C, 68.08; H, 4.86. Found: C, 68.42; H, 4.67.

sulting solution was made basic with sodium carbonate solution. The white crystals which appeared were filtered and recrystallized from Methyl Cellosolve.

α-3,4-Dimethoxyphenyl-β(3-indolyl)acrylonitrile. A mixture of 8.9 g. (0.05 mole) of 3,4-dimethoxyphenylacetonitrile and 7.3 g. (0.05 mole) of indole-3-aldehyde was refluxed in 200 ml. of absolute ethanol in the presence of 10 ml. of piperidine for 18 hr. On cooling, a precipitate appeared which was filtered and recrystallized from Methyl Cellosolve.

α-3,4-Dimethoxyphenyl-β(9-julolidyl)acrylonitrile. A mixture of 20.1 g. (0.1 mole) of julolidine-9-carboxaldehyde,[2] 17.7 g. (0.1 mole) of 3,4-dimethoxyphenylacetonitrile and 5.6 g. (0.1 mole) of potassium hydroxide in 200 ml. of absolute ethanol was refluxed. Crystals of the product began appearing in 5 min. and after 0.5 hr. the heating was stopped, 100 ml. of water was added and the flask cooled in an ice bath. The yellow product was filtered and recrystallized from Methyl Cellosolve-water.

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Infrared Spectrum of Tetra-*t*-Butylstilbenequinone

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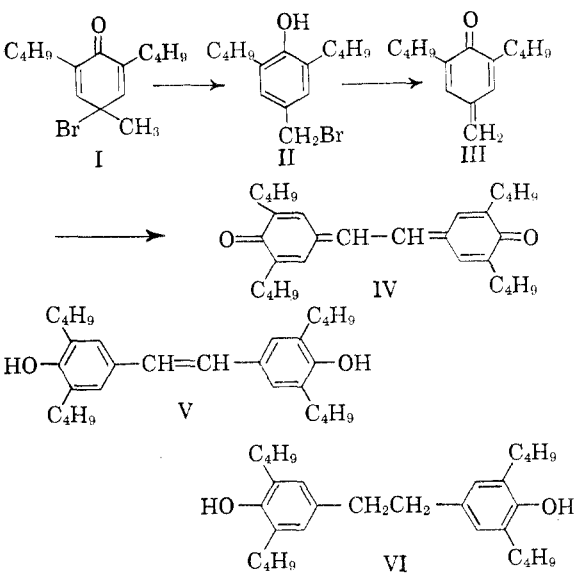
2,6-Di-*t*-butyl-*p*-cresol reacted with bromine to give I, a cyclohexadienone derivative[1] which rearranged on distillation[1,2] to the benzyl bromide II. Compound II was treated with tertiary amines which removed the elements of HX to give the presumed intermediate III, which was isolated as tetra-*t*-butylstilbenequinone.



This bright orange quinone was reduced to the corresponding diphenols (V) and (VI) by zinc-acetic acid, and lithium aluminum hydride, respectively.

The infrared absorption spectra of V and VI show a sharp "free" hydroxyl band at 2.75μ with no indication of any hydrogen-bonded hydroxyl even at relatively high concentrations. This results from the very effective steric hindrance provided by the adjacent *t*-butyl groups. The infrared spectrum of IV in $CHCl_3$ solution shows a remarkably large shift of the carbonyl band to 6.22 μ. For comparison, the carbonyl absorption in a $CHCl_3$ solution of 3,5,3′,5′-tetra-*t*-butyldipheno-

(1) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, 75, 734 (1953).
(2) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, 77, 1783 (1955).