graphed over 25 g. of alumina. The petroleum ether eluates yielded 43 mg. of a colorless oil whose infrared spectrum was identical with that of liquid *cis*-ketone III.[2a] None of the further eluates revealed the presence of any *trans*-ketone IIa.

A mixture of 100 mg. of the crude product from the hydrogenation of Ic, 10 ml. of concentrated hydrochloric acid and 10 ml. of methanol was refluxed for 12 hr. The cooled mixture was poured into 25 ml. of water and extracted with chloroform. The extract was washed with 10% sodium bicarbonate solution, dried over magnesium sulfate and the solvent evaporated. The remaining gum, 56 mg., was chromatographed on alumina. The early petroleum ether eluates yielded a colorless oil whose infrared spectrum proved it to be *cis*-ketone III, while the later petroleum ether fractions gave a solid, m.p. 104°, whose infrared spectrum was identical with that of *trans*-ketone IIa.

A mixture of 75 mg. of pure ketoester Ic, 5 ml. of concentrated hydrochloric acid and 7 ml. of ethanol was refluxed for 18 hr. After dilution of the cooled reaction mixture with 50 ml. of water, saturation with sodium chloride and extraction with chloroform, the combined extracts were dried over magnesium sulfate and evaporated to dryness. Crystallization of the slowly crystallizing residue from petroleum ether gave 37 mg. (63%) of a solid, m.p. 98–103°, which on recrystallization from the same solvent proved to be *trans*-ketone IIc, m.p. 107–108°, identical infrared spectrum with that of an authentic sample.[2a]

Methylation of Ib.—A solution of 200 mg. of Ib in 100 ml. of *t*-butyl alcohol was added to a stirred, nitrogen-blanketed solution of 35 mg. of potassium in 100 ml. of *t*-butyl alcohol. After 10 min. of stirring 3.0 ml. of methyl iodide was added. Thereupon the solution was refluxed for three hours, cooled, filtered and the filtrate evaporated to dryness. The residue was taken up in chloroform and water, the chloroform layer separated and the aqueous phase extracted twice with chloroform. The combined extracts were dried over anhydrous magnesium sulfate and evaporated to dryness. Trituration of the crystalline residue with petroleum ether yielded 110 mg. of a solid, m.p. 153–156°, which on four recrystallizations from methanol gave colorless prisms of VII, m.p. 157–158°; spectra: ultraviolet, λ_{max} 239 mμ (ϵ 15,000); infrared (CCl_4), C=O 5.79(s), 5.98(s) μ, C=C 6.12(m) μ.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.89; H, 7.44.

Desoxygenation of the Ketoesters Ic and IIc.—A mixture of 510 mg. of Ic, 0.5 ml. of ethanedithiol, 510 mg. of freshly fused zinc chloride, 1.02 g. of anhydrous sodium sulfate and 20 ml. of anhydrous benzene was stirred at room temperature for 48 hr. The mixture then was taken up in ether and water, the organic layer separated and washed twice with 5% sodium hydroxide solution and once with water. The organic extracts were dried over magnesium sulfate, the solvent evaporated and the resulting yellow gum chromatographed over 15 g. of alumina. Elution with benzene gave 490 mg. (74%) of a solid, m.p. 120–122°, which yielded colorless prisms of thioketal XVIII, m.p. 124.5–125.5°, after three crystallizations from aqueous methanol; spectra: ultraviolet, λ_{max} 272 mμ (ϵ 990), strong end absorption in the 220 mμ region; infrared (CCl_4), C=O 5.82(s) μ.

Anal. Calcd. for $C_{19}H_{22}O_2S_2$: C, 65.88; H, 6.40. Found: C, 66.09; H, 6.26.

A mixture of 490 mg. of XVIII, 1 g. of Raney nickel and 25 ml. of ethanol was refluxed for 12 hr. After filtration of the nickel the solution was evaporated to dryness and the remaining 306 mg. of colorless oil chromatographed on 5 g. of alumina. Petroleum ether elution yielded 244 mg. (68%) of liquid olefinic ester XIX; spectra: ultraviolet, λ_{max} 265 mμ (ϵ 720) and 272 mμ (ϵ 575), strong end absorption in the 220 mμ region; infrared (CCl_4), C=O 5.82(s) μ.

A mixture of 100 mg. of IIc, 0.1 ml. of ethanedithiol, 100 mg. of freshly fused zinc chloride, 200 mg. of anhydrous sodium sulfate and 10 ml. of benzene was stirred at room temperature for 48 hr. The reaction mixture then was filtered, the filtrate washed with 5% sodium hydroxide solution, dried over magnesium sulfate and evaporated. The residue was crystallized from petroleum ether to give 94 mg. of a solid, m.p. 163–166°. Evaporation of the mother liquors, chromatography of the residue over 5 g. of alumina and elution with 10:1 petroleum ether–ether led to an additional 10 mg. of the same solid, m.p. 165–167°. Four crystallizations from petroleum ether yielded colorless prisms of thioketal XVI, m.p. 165.5–166.5°; infrared spectrum (CCl_4), C=O 5.78(s) μ.

Anal. Calcd. for $C_{19}H_{24}O_2S_2$: C, 65.50; H, 6.94. Found: C, 65.18; H, 7.06.

A mixture of 160 mg. of XVI, 2 g. of Raney nickel and 15 ml. of ethanol was refluxed for 10 hr. After filtration of the nickel and evaporation of the solvent under vacuum a petroleum ether solution of the crude product was passed through a short alumina column. Elution with the same solvent yielded 105 mg. (88%) of liquid ester XVIIa; infrared spectrum (CCl_4), C=O 5.78(s) μ.

A mixture of 75 mg. of XVIIa, 10 ml. of 10% sodium hydroxide solution and 10 ml. of ethanol was refluxed for 8 hr. The reaction mixture then was diluted with 100 ml. of water and extracted with chloroform. The aqueous solution was acidified with hydrochloric acid and extracted with chloroform. The latter extract was dried over magnesium sulfate, the solvent evaporated and the crude product crystallized from methanol–water, giving 43 mg. (61%) of solid. Three recrystallizations from aqueous methanol led to colorless needles of the acid XVIIb, m.p. 153–154°; infrared spectrum (CCl_4), OH 2.83(w), 3.30(m) μ and shoulders at 3.07(w) and 3.14(m) μ; C=O 5.75(w), 5.89(s) μ.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.42.

Ames, Iowa

[Contribution from the Fundamental Research Department, the National Cash Register Co.]

Photochromic Spiropyrans. I. The Effect of Substituents on the Rate of Ring Closure

By Elliot Berman,* Richard E. Fox and Francis D. Thomson

Received May 16, 1959

The thermal formation of a number of 1,3,3-trimethylindolinobenzopyrylospirans, spiro-(2'H,1'-benzopyran-2,2'-(1,3,3-trimethylindolines)), from their "open form" precursors has been studied spectrophotometrically in ethanol at 6°. The dependence of the rate of ring closure on substituent shows good agreement with the Hammett equation.

Photochromic spiropyrans have been previously investigated notably by Bloch-Chaudé[1] and Hirshberg.[2] These authors have studied both the thermochromic and photochromic phenomena associated with this class of compounds. Our interest in these materials stems from their potential application to chemical systems for data storage.[3]

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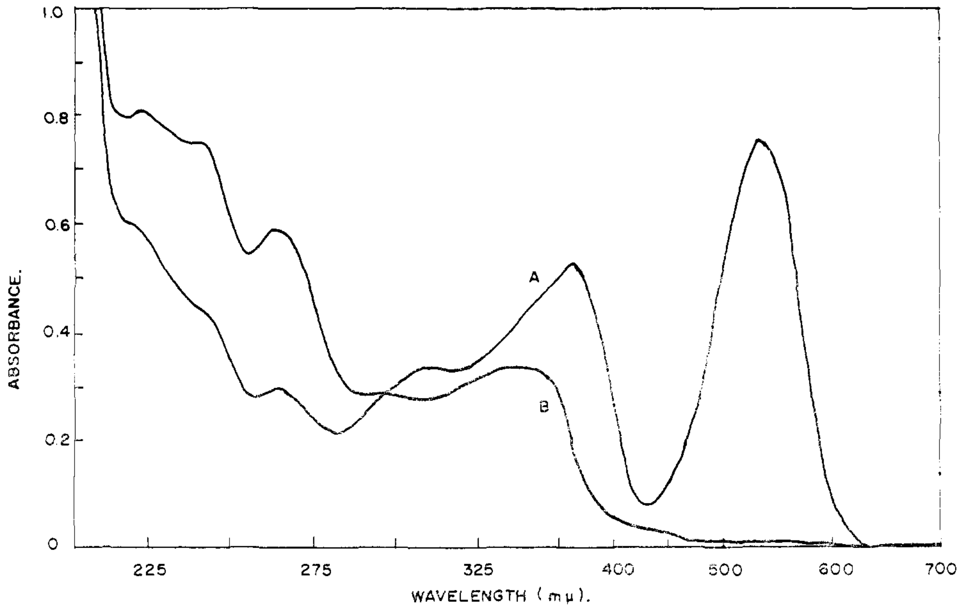
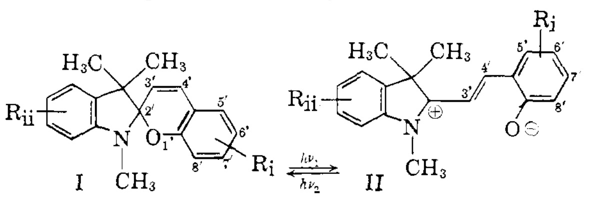


Fig. 1.—Spectra of 3.1×10^{-5} *M* solution of 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran in ethanol at 6°: curve A, after exposure to ultraviolet; curve B, before exposure.



Use of the photochemical system in data storage requires that states I and II should be reasonably stable at ordinary temperatures in the absence of provoking illumination and that photochemical interconversion of states I and II should also be possible at ordinary temperatures. Through work in these laboratories, spiropyrans which are photochemically active at room temperature and above have been developed, but until recently the thermal instability of state II excluded their use in practical data storage devices. We have found that the thermal stability of state II can be increased by discrete choice of substituents without apparent adverse effect on the photochemical process. As a quantitative measure of the thermal stability of II the rate constant for the dark reaction II → I has been determined. The rates are found to differ by more than one thousand fold with different substituents. The rates can be correlated with substituents by applying the Hammett equation.

Results

The rate of ring closure (II → I) was measured at 6° in absolute ethanol for twelve substituted 1,3,3-trimethylindolinobenzopyrylospirans by following the disappearance of the absorption band in the 500–600 mμ region. Figure 1 gives the ultraviolet and visible absorption spectra for 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran in the colorless state (I), curve B, and in the colored state (II), curve A. The absorption curve for state II represents a mixture of ring closed and ring opened materials at the photochemical steady state. Table I summarizes the rate data obtained by exposing a solution of the colorless photochromic spiropyran to ultraviolet light and following the rate of disappearance of the resultant visible absorption band. In all cases, the rates appear to follow good first-order kinetics. The rate constants in Table I are based on at least two runs at different concentrations. When necessary, the constants were obtained by a least square treatment of the data. The collection of rate constants in Table I shows clearly that the stability of the open form depends markedly on the substituents present. In the compounds studied, the rate constant for closure ranged from 1.3×10^{-2} for the 6′-methoxy-8′-nitro compound to 6.3×10^{-6} for the 6′-nitro-8′-fluoro compound.

Table I

Rate Constants for Thermal Stability and Sigma Values of Substituted 1,3,3-Trimethylindolinobenzopyrylospirans

Substituent	$\Sigma\sigma^a$	k, sec.$^{-1}$ (ethanol 6°)^c
6′-Nitro	0.79	4.28×10^{-5}
7′-Nitro	.67	7.11×10^{-5}
7′-Chloro	.40	1.26×10^{-3}
6′,8′-Dibromo	.36	3.97×10^{-3}
6′-Nitro-8′-allyl	.62^b	2.10×10^{-4}
6′-Nitro-8′-fluoro	1.03	6.33×10^{-6}
6′-Chloro-8′-nitro	0.91	2.27×10^{-5}
6′-Bromo-8′-nitro	.95	1.70×10^{-5}
6′-Nitro-8’-methoxy	.37	5.53×10^{-4}
6′-Methoxy-8′-nitro	.01	1.32×10^{-2}
5′-Nitro-8′-methoxy	.28	2.52×10^{-3}
6′-Nitro-8′-bromo	1.00	3.67×10^{-6}

[a] It is assumed that the unsaturated side chain *ortho* to the phenoxide group makes an equal sigma contribution in all compounds; this contribution is not included in $\Sigma\sigma$. [b] σ^*-value of methyl used for allyl. [c] The rate constant for the dark reaction I → II is neglected.[1]

An attempt was made to correlate rate of thermal reversal with substituent. It was found that using

TABLE II

SUBSTITUTED 1,3,3-TRIMETHYLINDOLINOBENZOPYRYLOSPIRANS

Substituent	M.p., °C.	Color of melt	Yield, %	Formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
6'-Nitro	176–177	Purple	89	$C_{19}H_{18}N_2O_3$	70.8	5.6	70.5	5.6
7'-Nitro	107–108	Orange	92	$C_{19}H_{18}N_2O_3$	70.8	5.6	70.6	5.8
7'-Chloro	116–117	Purple	74	$C_{19}H_{18}NOCl$	73.2	5.8	73.2	5.5
6',8'-Dibromo	115–116	Blue	84	$C_{19}H_{17}NOBr_2$	52.4	3.9	52.3	3.9
6'-Nitro-8'-allyl	108–109	Purple	87	$C_{22}H_{21}N_2O_3$	73.1	5.9	73.3	6.0
6'-Nitro-8'-bromo	255–256	Purple	88	$C_{19}H_{17}N_2O_3$	56.9	4.3	56.9	4.5
6'-Nitro-8'-fluoro	302–304	Purple	90	$C_{19}H_{17}N_2O_3F$	67.1	5.0	67.4	5.0
6'-Chloro-8'-nitro	134–135	Purple	86	$C_{19}H_{17}N_2O_3Cl$	64.0	4.8	64.3	4.8
6'-Bromo-8'-nitro	122–123	Purple	80	$C_{19}H_{17}N_2O_3Br$	56.9	4.3	56.9	4.3
6'-Nitro-8'-methoxy	152.5–153.5	Dk. blue	90	$C_{20}H_{20}N_2O_4$	68.2	5.7	68.2	6.0
6'-Methoxy-8'-nitro	116–117	Green	84	$C_{20}H_{20}N_2O_4$	68.2	5.7	67.8	5.9
5'-Nitro-8'-methoxy	166–167	Dk. green	91	$C_{20}H_{20}N_2O_4$	68.2	5.7	68.1	5.8

Brown's[4] σ^+-relationship for *meta* and *para* positions and Taft's[5] σ^*-values for the *ortho* positions gave reasonable correlation as indicated in Fig. 2.

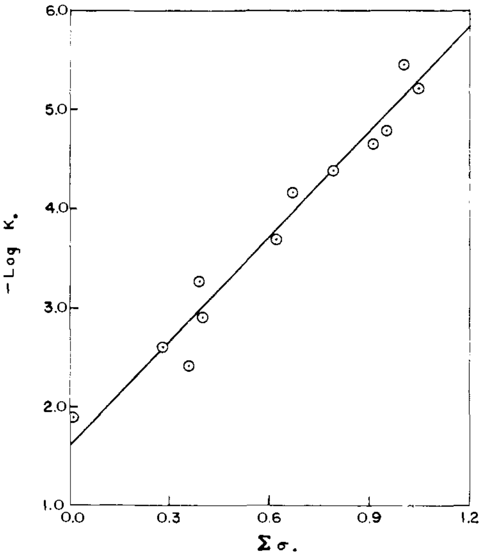


Fig. 2.—Rate *versus* sigma value for substituted 1,3,3-trimethylindolinobenzopyrylospirans.

Solution of the Hammett equation[6]

$$\log k/k^0 = \rho\sigma$$

for the data in Fig. 2 gives a value of −3.47 for the reaction constant, ρ. The correlation between rates and substituent constants suggests that *ortho* values may be used in electrophilic reactions at least in this special steric case.

Further papers will deal with the effect of other substituents on thermal stability of the spiropyran, and an investigation of the photochemical behavior of the photochromic spiropyrans.

Experimental[7]

Salicylaldehydes.—3-Nitro-5-methoxysalicylaldehyde, m.p. 130–132°, and 3-fluoro-5-nitrosalicylaldehyde, m.p. 89–91°, were prepared by Thomason Chemicals, Inc., 25 Bryant St., Woburn, Mass. 5-Nitrosalicylaldehyde was commercial material used directly, m.p. 126–127°. 4-Chlorosalicylaldehyde[8] was prepared in 34% yield by a Reimer–Tiemann reaction with *m*-chlorophenol, m.p. 50–51°. 3,5-Dibromosalicylaldehyde[9] was obtained by bromination of salicylaldehyde, m.p. 83–84°. 3-Allyl-5-nitrosalicylaldehyde was synthesized by a Claisen rearrangement of the allyl ether of salicylaldehyde followed by nitration; m.p. 157–158°. *Anal.* Calcd. for $C_{10}H_9NO_4$: C, 58.0; H, 4.4. Found: C, 57.9; H, 4.2. 3-Nitro-5-chlorosalicylaldehyde[10] was prepared by nitration of 5-chlorosalicylaldehyde, m.p. 105–107°. 3-Nitro-5-bromosalicylaldehyde[11] was obtained by nitration of 5-bromosalicylaldehyde, m.p. 147–148°. 3-Methoxy-5-nitrosalicylaldehyde[12] was obtained by nitration

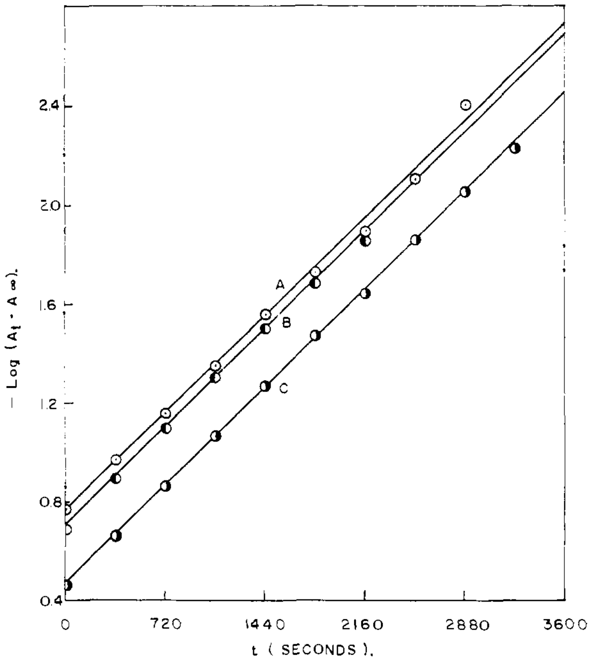


Fig. 3.—First-order rate plots for the disappearance of the colored form of 1,3,3-trimethylindolino-7'-chlorobenzopyrylospiran at 6° in ethanol.

Curve	A	B	C
k, sec.$^{-1}$	1.26×10^{-3}	1.27×10^{-3}	1.26×10^{-3}
concn. of colorless form before exposure, moles/l.	3.07×10^{-4}	7.67×10^{-4}	1.33×10^{-3}

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of *o*-vanillin, m.p. 141–142°. 3-Methoxy-6-nitrosalicylaldehyde[13] was synthesized by nitration of the benzenesulfonate of *o*-vanillin and then basic hydrolysis of the ester, m.p. 103–104°. 4-Nitrosalicylaldehyde, m.p. 133–134°, and 3-bromo-5-nitrosalicylaldehyde, m.p. 149–150°, were prepared at Boston University under the direction of Professors J. P. Mason and W. J. Gensler.

1,3,3-Trimethylindolinobenzopyrylospirans. General Directions.[14]—A mixture of equimolar amounts of the salicylaldehyde and commercially available 2-methylene-1,3,3-trimethylindoline in absolute ethanol (25 ml./0.01 mole of aldehyde) was refluxed on a steam-bath for two to five hours. The resultant highly colored mixture was cooled in an ice-water-bath, filtered, washed with cold ethanol, and recrystallized from ethanol or an ethanol–water mixture. The yields, melting points and elemental analyses for the compounds prepared are given in Table II.

Rate Measurements. Procedure.—The photochromic spiropyran was dissolved in absolute ethanol (U.S.I. Reagent Grade) and placed in a quartz, glass-stoppered spectrophotometer cell. The cell was placed in a cell holder equipped with a thermostat and allowed to come to thermal equilibrium. After 30 minutes, the temperature was measured by placing a thermocouple junction in the cell. The cell was then exposed to ultraviolet light from a four watt "Blak-Ray" (Ultra-violet Products Inc., San Gabriel, Calif.) or a 100 watt source (George W. Gates and Co., Long Island, N. Y.) for one to five minutes and immediately placed in either a Beckman DK-1 recording spectrophotometer or a Beckman DU spectrophotometer. The disappearance of the colored form of the photochromic spiran was followed automatically or manually by recording the absorbance at the maximum visible peak. The reaction was followed to 95–100% of completion. Absorbance at infinite time (A_∞) was zero or was taken as the absorbance after several days. Figure 3 gives results typical of those obtained.

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DAYTON 9, OHIO

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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rate Data and Isomer Distributions in the Reaction of *t*-Butylbenzene with Mercuric Acetate in Acetic Acid Solution. Partial Rate Factors for the Mercuration Reaction[1–3]

BY HERBERT C. BROWN AND M. DUBECK[4]

RECEIVED MARCH 21, 1959

The rate constants for the mercuration of *t*-butylbenzene with mercuric acetate in glacial acetic acid are (l. mole^{-1} sec.$^{-1}$) 8.40×10^{-5} at 90.0°, 1.52×10^{-5} at 70.0° and 0.245×10^{-5} at 50.0°. Substitution occurs predominantly in the *meta* and *para* positions, with substitution in the *ortho* position amounting to less than 1% of the total. The isomer distribution observed is 34.9% *m*-, 65.1% *p*- at 90.0°; 32.9% *m*-, 67.1% *p*- at 70.0°; 31.0% *m*-, 69.0% *p*- at 50.0°. Utilizing previously available data on the mercuration of benzene under these conditions, the following partial rate factors at 25.0° are calculated m_f 3.41, p_f 17.2. Consequently, in this reaction substitution *meta* to a *t*-butyl group occurs more readily than *meta* to a methyl group (m_f 2.23), whereas substitution *para* to a *t*-butyl group occurs less readily than *para* to a methyl group (p_f 23.0).

Different electrophilic substitution reactions result in major changes in the relative rates of reaction of the *meta* and *para* positions of toluene. The Selectivity Relationship (1) was proposed as a quantitative correlation of these data.[5]

$$\log p_f^{\mathrm{Me}} = \mathrm{b} \log (p_f^{\mathrm{Me}}/m_f^{\mathrm{Me}}) \qquad (1)$$

Data for some forty-seven electrophilic substitution reactions are now available. These data are correlated by the Selectivity Relationship with quite satisfactory precision.[6]

It was suggested that the Selectivity Relationship might be applicable to benzene derivatives other than toluene.[7] Unfortunately, with the exception of the detailed nitration data of Ingold and his co-workers,[8] the available data were far too sparse to permit a satisfactory test of this possibility.[9]

Accordingly, it appeared desirable to undertake a determination of the relative rates and isomer distributions in the substitution of several typical aromatic derivatives. As representative substitution reactions, we selected uncatalyzed mercuration,[10] acylation[11] and halogenation,[12] and applied them to *t*-butylbenzene and other selected aromatic compounds.

The results of the mercuration study with *t*-butylbenzene are presented in the present publication. The acylation[13] and halogenation[14] studies are reported in the following papers. In the final paper of this group,[15] the utility of the Selectivity Relationship in correlating all of the available substitution data for *t*-butylbenzene is examined.

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[1] Directive Effects in Aromatic Substitution. XXXVIII.

[2] This research supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

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