faintly positive and saponification, acidification, and steam distillation into bromine water did yield tribromophenol (0.16 g., 2%, m.p. 92°, mixture melting point undepressed). The reaction material after this treatment no longer gave a positive ester test. This reaction mixture was considered to be essentially entirely an acid mixture, however, by its behavior and infrared. The fact that not all of it was removed from the solvent by the alkaline wash is explained by the reluctance of acids like IV to be so extracted. They form soaps and emulsions, complicating such extraction techniques.

Triphenylbromoethylene (VII).—For comparison purposes (see above) this halide was prepared by the reaction of bromine in acetic acid with triphenylethylene (K & K Laboratories), as reported.[28] From the hydrocarbon (6.0 g., 0.0234 moles) the bromide was obtained as white needles (7.5 g., 97%), m.p. 117–118°, lit.[28] m.p. 115.5°, λ_{max}^{alc} 285 mμ (ε 9720). The infrared spectrum was in accord with the proposed structure and was identical with that of the halide isolated from the Cristol–Firth treatment of I (see above).

γ,γ,γ-Triphenylbutyryl Peroxide (X).—The acid IV was converted to its acid chloride in the usual fashion with thionyl chloride. The acid chloride (4.18 g., crude material *ca.* 12.5 mmoles) was added to dry ether (50 ml.) in which was suspended sodium peroxide (0.55 g., 7 mmoles). Three drops of water were added and the mixture was stirred at 0°. Another drop of water was added after each hour. After 2.5 hr., further sodium peroxide (*ca.* 0.1 g.) was added. After 3 hr., the initial yellow color (due to the sodium peroxide) had faded, whereupon the material was placed in the refrigerator overnight. Water (10 ml.) was added and the mixture was filtered at the pump. Acetone washes of the glassware were added to the collected precipitate, and the solution was allowed to evaporate in the air (4.05 g., quantitative yield). The peroxide was difficult to purify, but the following method afforded pure material, though with great loss. The crude peroxide above was treated with hot acetone (300 ml.), filtered from insoluble matter, and, while warm, diluted with water to cloudiness. The peroxide settled out on cooling as a white, microcrystalline solid (1.1 g., 28%), m.p. 116° dec. (on a block preheated to 100°), infrared 5.48 and 5.58 μ (peroxide C=O), iodometric titration gave a purity of >90%).

Anal.[29] Calcd. for $C_{44}H_{38}O_4$: C, 83.78; H, 6.07; O, 10.15. Found: C, 84.01; H, 6.06; O, 10.04.

Decomposition of the Peroxide X.—Several decompositions were carried out in the following way. A weighed amount of peroxide X (*ca.* 130 mg.) was refluxed in pure dry carbon tetrachloride (10 ml.) in a slow stream of nitrogen for 15 min., followed by 2-min. standing, with a previously tared Ascarite tube attached to the condenser. After the reaction, the Ascarite tube was reweighed to determine the carbon dioxide evolution. Evaporation (air) of the solvent left crystalline material which was then titrated for peroxide iodometrically. The results (averaged) indicated 39% carbon dioxide evolution (on the basis of 2 moles of carbon dioxide/mole of peroxide) and 67% peroxide recovered, implying (within error) essentially complete carbon dioxide evolution for the amount of peroxide reacted. From a decomposition carried out in the higher boiling solvent chlorobenzene, the entire reaction product was saponified and acidified. Steam distillation into bromine water indicated a trace (at most) of tribromophenol.

Conversion of γ,γ,γ-Triphenylpropyl Bromide (VI) to γ,γ,γ-Triphenylbutyronitrile.—The reaction product VI (1.8 g.), sodium cyanide (0.3 g.), and dimethyl sulfoxide (25 ml.) were heated with stirring at 130–140° for 50 min., at which time another 0.3 g. of sodium cyanide was added and the mixture heated 10 min. further. Addition of water and treatment of the ether phase in the usual way[8] gave the nitrile, which was recrystallized from ethanol (0.6 g., 40%), m.p. 135.5–137°, undepressed when admixed with the nitrile prepared from the iodide, infrared identical with that of the known.

(29) Galbraith Laboratories, Inc., Knoxville, Tenn.

Substituted γ-Lactones. XIII.[1] Nitration of Substituted α-Benzylidene-γ-butyrolactones

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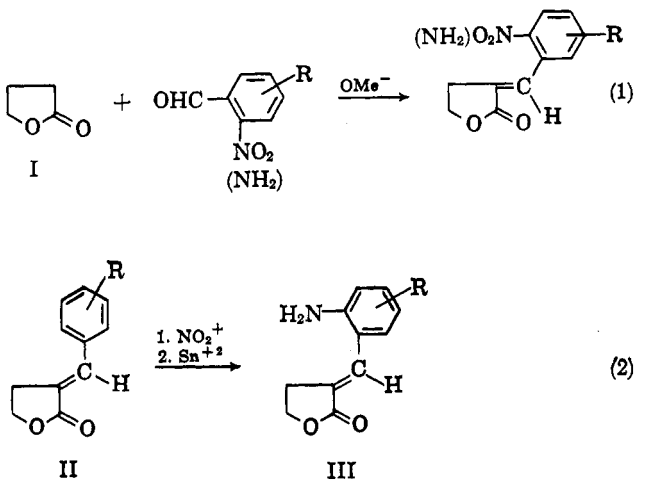
The nitration of various substituted α-benzylidene-γ-butyrolactones and -γ-valerolactones is reported. The substitution occurred generally at the same position where the corresponding benzoic acids and benzaldehydes were reported to undergo nitration. The factors influencing these electrophilic substitutions are discussed. The structures of the obtained nitro compounds were proved by oxidative degradation to the corresponding benzoic acids. Derivatives of the nitro compounds were prepared and some of their properties are reported.

Further exploration of a new rearrangement which α-(2-aminobenzylidene)-γ-butyrolactone (III) undergoes was attempted. This rearrangement was principally investigated as a convenient route toward a synthesis of dictamnine alkaloids.[1,4] Consequently, type III compounds with substituents like methoxy, ethoxy, and methylenedioxy were prepared. Two general methods for the synthesis of this type of compound are available: (1) condensation of the appropriate substituted benzaldehyde with γ-butyrolactone (I), or (2) nitration and reduction of an appropriate substituted α-benzylidene-γ-butyrolactone (II).

It was shown in a previous paper of this series[5] that the condensation of I with electron-withdrawing groups,



e.g., nitro or cyano groups, proceeded poorly or not at all. Attempts to use aminobenzaldehydes in this type of reaction led to excessive tar formation. Conse-

(1) Part XII: H. Zimmer and R. Walter, *Z. Naturforsch.*, **18b**, 669 (1963).

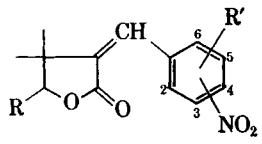
(2) National Institute of Health Fellow, 1961–1963.

(3) Postdoctoral Research Fellow, 1961–1963.

(4) (a) H. Zimmer, *Angew. Chem.* **73**, 144 (1961); 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961; (b) H. Zimmer, F. Haupter, J. Rothe, W. E. Schrof, and R. Walter, *Z. Naturforsch.*, **18b**, 165 (1963).

(5) H. Zimmer and J. Rothe, *J. Org. Chem.*, **24**, 28 (1959).

TABLE I



No.	R	Position of substituents 2	3	4	5	Position of NO_2 and derivatives	Formula	M.p., °C.	Solvent[a] of recrystn.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
1	H			OH		3	$C_{11}H_9NO_5$	161	M	56.17	55.85	3.86	4.26	5.96	6.28
2	H		OCH_2O			6	$C_{12}H_9NO_6$	183	M	54.80	54.83	3.51	3.45	5.30	5.39
3	H		OCH_2O			NH_2	$C_{12}H_{11}NO_4$	233–234	E	61.80	61.90	4.75	4.61	6.10	6.26
4	H		OCH_2O			$CNCH_2NH$	$C_{14}H_{12}N_2O_4$	203–205	M	61.79	62.14	4.44	4.71	10.29	10.01
5	H		OCH_2O			CH_3CONH	$C_{14}H_{13}NO_5$	257	E	61.09	61.14	4.76	4.59	5.09	5.06
6	H		OCH_2O			4-NO_2PhSO_2NH	$C_{18}H_{14}N_2O_8S$	268–269	DMF–M	51.68	49.85	3.35	3.37	6.70	6.59
7	H		OCH_2O			4-NH_2PhSO_2NH	$C_{18}H_{16}N_2O_6S$	244	E	55.67	55.61	4.15	4.21	7.21	7.37
8	H		OCH_2O			3,5-$NO_2PhCONH$	$C_{19}H_{13}N_3O_9$	289	E	53.40	53.52	3.07	3.19	9.83	9.82
9	H		OCH_2O			PhCH=N	$C_{19}H_{15}NO_4$	199	M	71.02	71.14	4.71	4.91	4.36	4.46
10	H			OCH_3		3	$C_{12}H_{11}NO_5$	161	M	57.83	56.91	4.45	4.52	5.62	5.74
11	H			OCH_3		NH_2	$C_{12}H_{13}NO_3$	180	M	65.74	66.60	6.97	6.22	6.39	6.30
12	H			OCH_3		CH_3CONH	$C_{14}H_{15}NO_4$	210	E	64.36	64.80	5.79	5.42	6.36	5.39
13	H			OCH_3		4-NO_2PhSO_2NH	$C_{18}H_{16}N_2O_7S$	199	E	53.47	53.69	3.99	3.98	6.93	7.14
14	H			OCH_3		$PhSO_2NH$	$C_{18}H_{17}NO_5S$	189	E	60.16	60.42	4.77	4.79	3.90	4.30
15	H			OCH_3		4-NH_2PhSO_2NH	$C_{18}H_{18}N_2O_5S$	198	D–P	57.75	57.07	4.85	5.07	7.48	7.46
16	H			OCH_3		4-$AcNHPhSO_2NH$	$C_{20}H_{20}N_6O_6S$	265	DMF–Et	57.69	57.43	4.84	4.97	6.73	6.77
17	H	OCH_3	OCH_3				$C_{13}H_{14}O_4$	92	M	66.66	67.14	6.02	6.02		
18	H	OCH_3	OCH_3			5	$C_{13}H_{13}NO_6$	219	M	55.91	56.19	4.70	4.46	5.02	5.01
19	H	OCH_3	OCH_3			NH_2	$C_{13}H_{15}NO_4$	159	M	62.64	62.22	6.07	6.13	5.62	5.71
20	H	OCH_3	OCH_3			CH_3CONH	$C_{15}H_{17}NO_5$	188–189	M	61.85	61.05	5.88	6.10	4.81	4.74
21	H	OCH_3	OCH_3			PhCH=N	$C_{20}H_{19}NO_4$	127–128	M	71.20	71.20	5.68	5.75	4.15	4.22
22	H			CH_3			$C_{12}H_{12}O_2$	104–105[b]	M	76.57	76.32	6.43	6.31		
23	H			CH_3		3	$C_{12}H_{11}NO_4$	125–126	M	61.80	62.32	4.75	4.94	6.01	6.13
24	H	OCH_3			OCH_3		$C_{13}H_{14}O_4$	97	M	66.66	66.45	6.02	5.84		
25	H	OCH_3			OCH_3	4	$C_{13}H_{13}NO_6$	182	M	55.91	55.66	4.70	4.73	5.02	5.36
26	H	OCH_3			OCH_3	NH_2	$C_{13}H_{15}NO_4$	214–215	M	62.64	62.62	6.07	6.11	5.62	5.64
27	H	OCH_3			OCH_3	CH_3CONH	$C_{15}H_{17}NO_5$	244–245	M	61.85	62.15	5.88	6.04	4.81	4.86
28	H		OCH_3	OCH_3		6	$C_{13}H_{13}NO_6$	165	M	55.91	55.57	4.70	4.70	5.02	5.10
29	H		OCH_3	OCH_3		NH_2	$C_{13}H_{15}NO_4$	162	M	62.64	62.41	6.07	6.19	5.62	6.10
30	H		OCH_3	OCH_3		CH_3CONH	$C_{15}H_{17}NO_5$	169–170	M	61.85	60.54	5.88	5.77	4.81	4.92
31	H		OCH_3	OCH_3		4-NO_2PhSO_2NH	$C_{19}H_{18}N_2O_8S$	234	D–P	52.54	52.60	4.18	4.97	6.45	5.80

32	H	OCH_3	OCH_3	$PhSO_2NH$	$C_{19}H_{19}NO_6S$	231	M	58.61	59.12	4.92	4.97	3.60	3.00
33	H	OCH_3	OCH_3	$4\text{-}NH_2PhSO_2NH$	$C_{19}H_{20}N_2O_6S$	235	D–P	56.43	56.14	4.99	4.88	6.93	6.71
34	H	OCH_3	OCH_3	$4\text{-}AcNHPhSO_2NH$	$C_{21}H_{22}N_2O_7S$	250	D–P	56.50	55.60	4.97	5.02	6.28	5.90
35	H	OC_2H_5	OC_2H_5	6	$C_{15}H_{17}NO_6$	171	E	58.63	58.33	5.58	5.42	4.56	4.61
36	H	OC_2H_5	OC_2H_5	NH_2	$C_{15}H_{19}NO_4$	149–150	E	64.96	64.71	6.91	6.83	5.05	5.08
37	H	OC_2H_5	OC_2H_5	CH_3CONH	$C_{17}H_{21}NO_5$	205–206	M	63.93	62.62	6.63	6.40	4.39	3.92
38	H	OC_2H_5	OC_2H_5	$PhCH{=}N$	$C_{22}H_{23}NO_4$	102–104	M	72.31	71.51	6.34	6.04	3.83	4.00
39	CH_3	Cl	Cl		$C_{12}H_{10}Cl_2O_2$	105	M	56.06	56.00	3.92	4.00		[c]
40	CH_3	Cl	Cl	6	$C_{12}H_9Cl_2NO_4$	169–170	M	47.7	47.61	3.00	3.09	4.64	4.80[d]
41	CH_3	OCH_2O		6	$C_{13}H_{11}NO_6$	168	M	56.32	56.27	4.00	3.88	5.05	5.37
42	CH_3	OCH_2O		NH_2	$C_{13}H_{13}NO_4$	174	M	63.15	63.34	5.30	5.28	5.67	5.89
43	CH_3	OCH_2O		$CNCH_2NH$	$C_{15}H_{14}N_2O_4$	195–196	M	62.93	63.48	4.93	4.98	9.76	10.18
44	CH_3	OCH_2O		CH_3CONH	$C_{15}H_{15}NO_5$	197	M	62.28	61.93	5.23	5.34	4.84	5.23
45	CH_3	OCH_2O		$3,5\text{-}(NO_2)_2PhCONH$	$C_{20}H_{15}N_3O_9$	219–220	E	54.43	54.55	3.43	3.46	9.52	9.69
46	CH_3	OCH_2O		$PhCH{=}N$	$C_{20}H_{17}NO_4$	164–165	M	71.63	71.54	5.11	5.18	4.18	4.08
47	CH_3	OCH_2O		$PhCONH$	$C_{20}H_{17}NO_5$	235	E	68.37	68.27	4.88	4.98	3.99	3.58
48	CH_3	OC_2H_5	OC_2H_5		$C_{16}H_{20}O_4$	108–109	M	69.54	69.37	7.30	7.08	...	...
49	CH_3	OC_2H_5	OC_2H_5	6	$C_{16}H_{19}NO_6$	144–145	M	59.80	59.63	5.96	5.91	4.36	4.56
50	CH_3	OC_2H_5	OC_2H_5	NH_2	$C_{16}H_{21}NO_4$	196	M	65.95	66.03	7.27	7.46	4.81	4.84
51	CH_3	OC_2H_5	OC_2H_5	$PhCH{=}N$	$C_{23}H_{25}NO_4$	137	M	72.80	72.82	6.64	6.75	3.69	3.73

[a] D = dioxane, DMF = dimethylformamide, E = ethanol, Et = diethyl ether, M = methanol, P = petroleum ether. [b] Compound 22 has been published by H. Zimmer and J. Rothe [*J. Org. Chem.*, **24**, 28 (1959)], but the melting point was reported as 63–64°. [c] *Anal.* Calcd.: Cl, 27.58. Found: Cl, 27.81. [d] *Anal.* Calcd.: Cl, 23.47. Found: Cl, 23.59.

quently, route 1 was not used. Route 2, on the other hand, appeared much more promising for obtaining the desired class of compounds, since it previously was shown[6] that nitration of II led to a mixture of α-(2- and 4-nitrobenzylidene)-γ-butyrolactone which easily could be separated and then reduced to III (and the 4 isomer). This showed that the α-methylidene group in I possessed activating properties and, therefore, caused *ortho* and *para* orientation in electrophilic aromatic substitution. Therefore, it was hoped to obtain some *o*-nitro isomers as reaction products of the nitration of substituted II. This paper describes in some detail the results of the nitration of several type II compounds substituted by hydroxy, methoxy, ethoxy, methylenedioxy, chloro, and methyl groups.

Results and Discussion

The usual nitration procedures employing HNO_3–H_2SO_4 or H_2SO_4–KNO_3 which were applied in the nitration of II[6] did not work with the substituted type II compounds used in this study. Instead, only tars were obtained. Nitration, however, was accomplished with concentrated nitric acid (*d* 1.42) as nitrating agent. Care was taken that the temperature did not rise over 0–5°. Best results were achieved at about −10°, when yields of 95–100% of nitration product were obtained. On the other hand, type II compounds substituted by deactivating groups needed fuming nitric acid for nitration. Through the introduction of one nitro group the phenyl ring became so deactivated that under the elected conditions no further nitration took place. In Table I the compounds obtained by these nitrations are reported along with some of their derivatives.

The nitration occurred nearly always at the same position at which the corresponding benzoic acids or benzaldehydes were reported to undergo nitration. This can be readily explained by assuming that the strong electron-donating groups on the phenyl ring as used in this study were the only ones which exerted an orientation upon the incoming nitro group and, therefore, take preference over the weak *ortho–para* orientation power of the methylidene group. In Table II the results of nitration are reported and the findings are compared with the behavior of the corresponding benzoic acids and benzaldehydes under these conditions.

The only exception was compound 25. In this case, however, the deviation from the normal behavior can be accounted for by steric hindrance with the α-methylidene-γ-butyrolactone group possessing larger spatial requirements than either the carboxylic acid or the carboxaldehyde groups. In agreement with this assumption is the fact that α-(3,4,5-trimethoxybenzylidene)-γ-butyrolactone could not be nitrated, whereas the nitration of 3,4,5-trimethoxybenzoic acid was reported to take place at the 2-position.[7,8]

Compound 24 was expected to undergo nitration at 6-position. This is analagous to 2,5-dimethoxybenzoic acid, which was reported to have been nitrated, yielding the 6- and 3-nitro derivatives[9]; however, 24 underwent nitration at the 4-position. This is also in agreement

(6) H. Zimmer and J. Rothe, *J. Org. Chem.*, **24**, 100 (1959).
(7) J. Pollak and H. Feldscharek, *Monatsh.*, **29**, 139 (1908).
(8) J. Harding, *J. Chem. Soc.*, **99**, 1585 (1911).
(9) See under *k*, Table II.

TABLE II

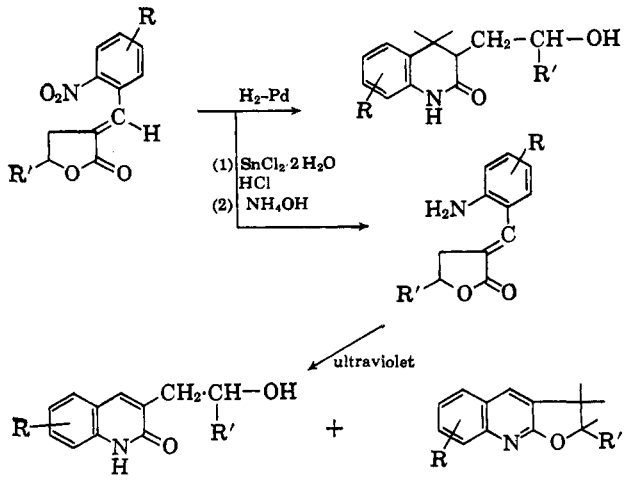
No. of compound in Table I	Position of nitration in corresponding benzoic acid	Ref.	Position of nitration in corresponding benzaldehyde	Ref.	Agreement of nitration position with substituted II
1	3	*a*	3	*b*	Yes
2,41	6	*c*	6	*d*	Yes
10	3	*e*		*f*	Yes
18	5	*g*	5,6	*h*	Yes
22	3	*i*	3	*j*	Yes
25	3,6	*k*	6,(3)	*k*	No
28	6	*l*	6	*m*	Yes
35,49	6	*n*	6	*o*	Yes
40	6	*p*	6	*q*	Yes

[a] See ref. 12. [b] M. Schöpff, *Ber.*, **24**, 3776 (1891); C. Paal, *ibid.*, **28**, 2413 (1895), and further references; K. Auwers and H. Röhrig, *ibid.*, **30**, 996 (1897). [c] See ref. 13. [d] R. Fittig and J. Remsen, *Ann.*, **159**, 134 (1871); F. Haber, *Ber.*, **24**, 624 (1891); G. Ciamician and P. Silber, *Gazz. chim. ital.*, **33I**, 371 (1903); A. H. Salway, *J. Chem. Soc.*, **95**, 1163 (1909); M. T. Bogert and F. R. Elder, *J. Am. Chem. Soc.*, **51**, 534 (1929). [e] See ref. 14. [f] A. Einhorn and J. P. Grabfield, *Ann.*, **243**, 370 (1880); E. Worner, *Ber.*, **29**, 157 (1896); M. P. De Lang, *Rec. trav. chim.*, **45**, 45 (1926). [g] See ref. 15. [h] W. H. Perkin, R. Robinson, and F. W. Stoyle, *J. Chem. Soc.*, **125**, 2357 (1924). [i] R. Fittig, and W. Ramsay, *Ann.*, **168**, 251 (1873); E. Kloppel, *Ber.*, **26**, 1733 (1893); M. L. van Scherpenzeel, *Rec. trav. chim.*, **20**, 158 (1901). [j] L. Gattermann, *Ann.*, **347**, 354 (1906); V. Hanzlik, and A. Bianchi, *Ber.*, **32**, 1288 (1899). [k] See ref. 10. [l] W. Merch, *Ann.*, **108**, 54 (1858); F. Tiemann and K. U. Matsmoto, *Ber.*, **9**, 938 (1876); Th. Zincke and B. Francke, *Ann.*, **293**, 177 (1897). [m] R. Pschorr and C. Sumuleanu, *Ber.*, **32**, 3412 (1899). [n] This study. [o] J. Szabo and E. Vinkler, *Acta Chim. Sci. Hung.*, **17**, 201 (1958). [p] See ref. 19. [q] Höchster Farbwerke, German Patent 254,467; A. Claus and A. W. Bücher, *Ber.*, **20**, 1624 (1887)

with the nitration of ω-bromo-2,5-dimethoxyacetophenone, which upon nitration yielded the 4-nitro derivative along with the 6-nitro isomer.[10]

The position at which the nitration took place on type II compounds was generally determined by potassium permanganate oxidation, which yielded the corresponding benzoic acid. All these acids were known compounds; in a few instances in which there were only scanty literature references available, the structures of the resulting benzoic acids were further confirmed by their n.m.r. spectra. Additional proof for the position of nitration was provided in the following ways. First, the type II compound was hydrogenated to yield the α-aminobenzyl-γ-lactone derivative, or, in cases in which nitration took place *ortho* to the methylidenelactone group, the corresponding 2-oxo-1,2,3,4-tetrahydroquinoline.[11] Secondly, only the nitro group was reduced to the amino group. Again, if the nitro group occupied the *ortho* position, type III compound could be rearranged by ultraviolet radiation[4] in alcoholic solution to yield the corresponding 2-oxoquinoline, the corresponding furoquinoline, or both products (Scheme I; details will be published in a forthcoming communication).

SCHEME I



(10) R. W. Bost and C. A. Howe, *J. Am. Chem. Soc.*, **73**, 5864 (1951).
(11) H. Zimmer and R. Walter, *Naturwiss.*, **50**, 331 (1963).

Experimental

Melting points are uncorrected. Microanalyses by A. Bernhardt, Mikroanalytisches Laboratorium in Max-Planck Institute, Mühlheim/Ruhr, Germany, and Aug. Peisker-Ritter, Mikroanalytisches Laboratorium, Brugg, Switzerland.

Condensations.—The condensations were run as described in literature.[5]

Nitrations. A. Nitration of α-Benzylidene-γ-butyrolactones with Activating Substituents in the Phenyl Group.—A solution of 250 ml. of nitric acid (*d* 1.42) was cooled by means of an ice–salt bath. While being stirred 50–80 g. of carefully powdered and dried α-benzylidene-γ-butyrolactone species was added. The internal temperature was held for the next 4 hr. at −10° and then permitted to rise to +5°. Nitration took place even though in some cases solution was not complete. The mixture was poured into 1000 ml. of water. A yellow precipitate occurred, which was filtered by suction and thoroughly washed with cold water and ice-cold ether. Recrystallization either from methanol or ethanol was performed.

B. Nitration of α-Benzylidene-γ-butyrolactones without Activating Substituents in the Phenyl Group.—A solution of 50 ml. of fuming nitric acid was cooled with ice and 5 g. of the carefully powdered compound was added keeping the temperature below +5°. After 30 min. the mixture was diluted with 150 ml. of water. It was treated further as described in A.

Verification of the Nitration Products. General Procedure. A. Verification of the Structures of the Compounds 1, 10, 18, 22, 25, 28, 35, and 49 (Table I).—To a suspension of 2 g. of α-nitrobenzylidene-γ-butyrolactone derivative in 300 ml. of water was added 7 g. of potassium permanganate. The temperature was held at 80–90° for 2–3 hr. The manganese dioxide was filtered off and the hot yellow solution was concentrated by evaporation to 50 ml. Acidification with 10% sulfuric acid gave free acid.

B. Verification of the Structures of the Compounds 2, 40, and 41.—The procedure was the same as A, except that the oxidation was performed at room temperature over a period of 4 hr. After acidification the solution was extracted with benzene, which was evaporated. The resulting oil was recrystallized from methanol. The melting points of these acids did agree with the ones reported in the literature, the only exception being 2,5-dimethoxy-4-nitrobenzoic acid. 3-Nitro-4-hydroxybenzoic acid was obtained from compound 1, m.p. 184–185°[12]; 6-nitro-3,4-methylenedioxybenzoic acid from compounds 2 and 41, m.p. 172°[13]; and 3-nitro-

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4-methoxybenzoic acid[14] from compound 10, m.p. 186–187°. 5-Nitro-2,3-dimethoxybenzoic acid[15] had m.p. 178°. The n.m.r. spectrum showed a 2.85-c.p.s. splitting of the aromatic protons which is further evidence for the assumed structure.

Anal. Calcd. for $C_9H_9NO_6$: N, 6.17. Found: N, 6.28.

3-Nitro-4-methylbenzoic acid[16] had m.p. 190°. 4-Nitro-2,5-dimethoxybenzoic acid had m.p. 198°, lit.[10] m.p. 192–193°.

Anal. Calcd. for $C_9H_9NO_6$: N, 6.17. Found: N, 6.18.

Hydrogenation gave α-(4-amino-2,5-dimethoxybenzyl)-γ-butyrolactone, m.p. 108°. The infrared spectrum showed absorption peaks corresponding to a primary amino group (2.98 and 3.08 μ) and a carbonyl group (5.67 μ). The n.m.r. spectrum is in agreement with aromatic protons occupying the positions *para* to each other.

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 63.65; H, 6.98; N, 5.59.

6-Nitro-3,4-dimethoxybenzoic acid[17] had m.p. 187° and 6-nitro-3,4-diethoxybenzoic acid[18] had m.p. 143–144°. 3,4-Diethoxybenzoic acid was nitrated at 0° with nitric acid (*d* 1.42); after purification it showed m.p. 144–145°. Mixture melting point with acid obtained by degradation showed no depression. 6-Nitro-3,4-dichlorobenzoic acid[19] had m.p. 164°.

Reduction of α-(Nitrobenzylidene)-γ-butyrolactones to α-(Aminobenzylidene)-γ-butyrolactones.—The general procedure has been published elsewhere.[5] It was altered so that only 180 ml. of hydrochloric acid was used and instead of chloroform in the Soxhlet extraction dry acetone was used. The advantage was that no tars occurred. All amines possessed a yellow color.

Schiff's Bases.—One-half gram of the appropriate amine was dissolved in 1 ml. of benzaldehyde and heated on the water bath for 30 min. Addition of 5 ml. of methanol and cooling in an ice bath caused precipitation of yellow needles. Recrystallization was performed from methanol.

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A Novel Synthesis of Nitroalkyl Ethers and Their Cleavage to Nitro Alcohols

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The reaction of 2-nitroalkyl acetates with alkali alkoxides and alkyl thiolates has been found to constitute a convenient route for the synthesis of 1-alkoxy-2-nitro alkanes and alkyl 2-nitroalkyl sulfides, respectively. Michael-type additions of 1-alkoxy-2-alkane nitronates to 2-nitro alkenes (prepared *in situ* from 2-nitroalkyl acetates) afford 1-alkoxy-2-alkyl-2,4-dinitro alkanes in satisfactory yields. Reaction of these nitro ethers with boron trichloride results in cleavage with the formation of 2-alkyl-2,4-dinitro 1-alkanols in good yield.

It has been well-established that the Michael-type addition of primary nitro alkanes to α-nitro alkenes gives the desired adducts only in poor yield.[2-6] On the other hand, the reaction affords high yields with secondary nitro alkanes. It seems, therefore, that in order to obtain good yields in the Michael-type addition with primary nitro alkanes, the latter should first be converted to secondary ones. Such a conversion is available readily in the methylolation reaction which converts primary nitro alkanes into secondary nitro alcohols.[7] However, at the basic conditions of the Michael-type addition, these nitro alcohols undergo demethylolation and cannot be employed satisfactorily. It was, therefore, the purpose of this investigation to convert the hydroxyl group in nitro alcohols into a group which would be stable under the conditions of the Michael-type addition, then to regenerate the hydroxyl group, and finally to convert by demethylolation the resulting polynitro alkanol into the polynitro alkane. While the first two goals of this research could be realized, the demethylolation step which required basic catalysis did not lead to the desired polynitro alkanes; instead, a rearrangement took place leading to isoxazoles.[8]

At the outset of this investigation it was hoped that acetals would be good protecting groups and would subsequently be removed readily. These expectations were, however, not fulfilled when tested on model compounds. For instance, 2-(2-nitro-2-methyl-1-propoxy)-tetrahydropyran which was prepared from dihydropyran and 2-nitro-2-methyl-1-propanol according to the procedure of Parham[9] could not be cleaved to the alcohol with dilute hydrochloric acid. Stronger acids such as concentrated hydrochloric acid or boron trichloride caused extensive tar formation. The acetal, bis(2-nitrobutoxy)methane[10] (I), was quantitatively converted to 2-nitro-1-butanol (II) by cleavage with boron trichloride but was found to be unstable at the conditions of the Michael-type reaction. I was readily hydrolyzed in basic medium to the alcohol (II) and formaldehyde.

$$\underset{\text{I}}{(H_3CCH_2CH(NO_2)CH_2O)_2CH_2} \xrightarrow{OH^-} \underset{\text{II}}{2H_3CCH_2CH(NO_2)CH_2OH} + CH_2O$$

Preparation of 1-Alkoxy-2-nitro Alkanes.—Because of the instability of nitroalkyl acetals at the conditions at which Michael-type additions are usually carried out, our investigation turned to 2-nitroalkyl ethers in which

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