Proportions of Isomers from Mononitration of 2,4,6-Trinitrobiphenyl (Picrylbenzene)

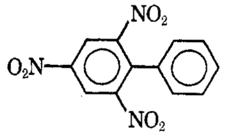
F. E. CONDON* AND J. P. TRIVEDI[1]

Department of Chemistry, The City College of the City University of New York, New York, New York 10031

Received November 12, 1970

The nitration of 2,4,6-trinitrobiphenyl (picrylbenzene) has been studied in order to ascertain the directive influence of the 2,4,6-trinitrophenyl (picryl) group in electrophilic aromatic substitution. The expected isomers, *o*-, *m*-, and *p*-nitropicrylbenzene, were synthesized by Ullmann reactions and were shown to be stable under the nitrating conditions used (solvent acetic acid at 100°, 2 hr). In an apparently novel use of Varian A-60 nmr spectrophotometer output, the composition of the nitration product was determined by matching its integrator curve with those of synthetic mixtures having nearly the same composition. The result was 8.0 ± 0.4% *o*-, 30.0 ± 0.8% *m*-, and 62.0 ± 0.8% *p*-nitropicrylbenzene.

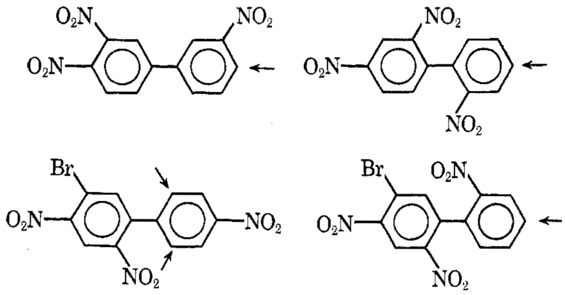
The nitration of 2,4,6-trinitrobiphenyl (**1**) is of interest in connection with the theory of orientation in electrophilic aromatic substitution, especially as it relates to biphenyl and its derivatives. Nitration of biphenyl[2] and its derivatives usually takes place chiefly ortho and para to a substituent phenyl group, even when the substituent phenyl group is loaded with meta-directing or electron-withdrawing substituents.[2b,3] The examples of Chart I are particularly relevant.[3l,o]



1

CHART I

PREFERRED POSITIONS FOR NITRATION OF SOME TRINITROBIPHENYLS



Exceptions occur when the ortho–para-directing influence of a chlorine or bromine is in competition with that of a nitrophenyl group, as in the examples of Chart II.[3i,k,m,n]

The orientation effect in biphenyl is attributable to effective delocalization of charge into the substituent phenyl group in the intermediate carbonium ion resulting from ortho or para attack[4] (Chart III). Such delocalization is not possible when the attack is in a position meta to the phenyl group. The examples of Chart II, however, indicate that a chlorine or bromine is better able to delocalize charge (by electron release) than a nitrophenyl group.

CHART II

PREFERRED POSITIONS FOR NITRATION SHOWING THAT THE ORTHO–PARA DIRECTING INFLUENCE OF A HALOGEN EXCEEDS THAT OF A NITROPHENYL GROUP

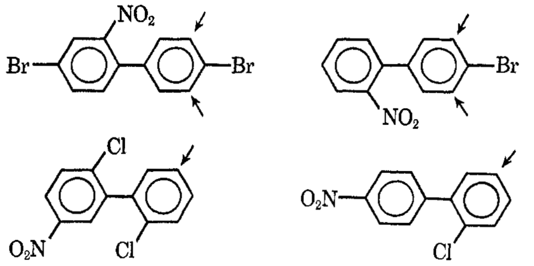
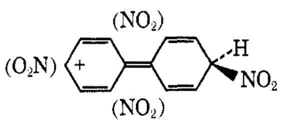


CHART III

ONE OF THE PRINCIPAL RESONANCE FORMS OF THE CARBONIUM ION INTERMEDIATE FOR NITRATION OF BIPHENYL (OR 2,4,6-TRINITROBIPHENYL), ILLUSTRATED WITH PARA ATTACK



The 2,4,6-trinitrophenyl, or "picryl," group occupies an extreme position among modified phenyl substituents, in that the nitro group is one of the most strongly deactivating and meta-directing substituents;[5] and in 2,4,6-trinitrobiphenyl the three nitro groups are so positioned that every resonance form of the intermediate making use of the trinitrophenyl group for charge delocalization has a strongly electron-withdrawing nitro group on the carbon bearing the positive charge (Chart III). The intermediates necessary for substitution ortho and para to the picryl group might be expected to be no more stabilized, therefore, than the intermediate for meta substitution, and the picryl group might be without any orienting influence on the

---

[1] On leave from St. Xavier's College, Ahmedabad, India.

[2] (a) M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford, *J. Chem. Soc.*, 3573, 3576 (1956); (b) Y. Mizuno and O. Simamura, *ibid.*, 3875 (1958).

[3] (a) H. C. Gull and E. E. Turner, *ibid.*, 491 (1929); (b) W. Blakey and H. A. Scarborough, *ibid.*, 3000 (1927); (c) W. S. M. Grieve and D. H. Hey, *ibid.*, 968 (1933); (d) H. G. Dennett and E. E. Turner, *ibid.*, 476 (1926); (e) R. J. W. Le Fèvre and E. E. Turner, *ibid.*, 2041 (1926); (f) R. J. W. Le Fèvre, D. D. Moir, and E. E. Turner, *ibid.*, 2330 (1927); (g) R. J. W. Le Fèvre and E. E. Turner, *ibid.*, 1158 (1930); (h) E. E. J. Marler and E. E. Turner, *ibid.*, 1359 (1931); (i) F. R. Shaw and E. E. Turner, *ibid.*, 285, 509 (1932); (j) E. E. J. Marler and E. E. Turner, *ibid.*, 266 (1937); (k) F. H. Case, *J. Amer. Chem. Soc.*, **64**, 1848 (1942); (l) F. H. Case, *ibid.*, **64**, 2225 (1942); (m) F. H. Case and R. U. Schock, Jr., *ibid.*, **65**, 2086 (1943); (n) F. H. Case, *ibid.*, **65**, 2137 (1943); (o) F. H. Case, *ibid.*, **67**, 116 (1945).

[4] (a) J. D. Roberts, R. A. Clement, and J. J. Drysdale, *ibid.*, **73**, 2181 (1951); (b) B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **75**, 1473 (1956).

[5] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press, New York, N. Y., 1959, pp 83–88.

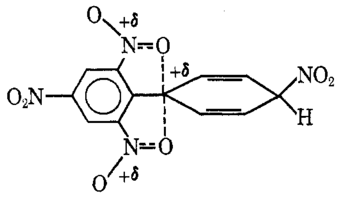
meta and para positions.[6] This would be an *electronic inhibition of resonance.*

Steric inhibition of resonance is also a possibility with the picryl group. Steric interference between the two ortho nitro groups and the two ortho hydrogens on the other ring might prevent the two rings from assuming the coplanar arrangement necessary for resonance stabilization of the intermediates for ortho and para substitution (Chart III). If this were completely effective, and excluding other possible effects, the picryl group would be without orienting influence on the meta and para positions, and statistics would lead one to expect twice as much meta as para product.[7]

It might be argued also that the picryl group should be a meta-directing group. With resonance inhibited electronically and sterically, there remains what may be a strong electron-withdrawing inductive effect, like that of the CF_3 group, which appears to be nearly 100% meta directing.[5,8] The effect of this would be to destabilize the intermediate carbonium ion resulting from ortho and para attack, thus favoring meta substitution.

The pathway pictured in Chart III requires that the benzene rings be coplanar for effective resonance participation by the picryl group. With the benzene rings in orthogonal planes, however, the ortho nitro group oxygens of the picryl substituent might be able to stabilize the carbonium ion resulting from ortho or para nitration through delocalization of charge by a field effect as shown in Chart IV. This pathway and the one pictured in Chart III are mutually exclusive because of the requirement that the rings be orthogonal for one and coplanar for the other. Thus, it might be possible to assess the relative importance of these two mutually exclusive pathways by experiments with a 2,6-disubstituted picrylbenzene, in which the pathway of Chart III is sterically excluded. Such experiments are planned for this laboratory, for which the results reported here are a necessary preliminary.

CHART IV
ALTERNATIVE PATHWAY FOR NITRATION OF 2,4,6-TRINITROBIPHENYL



Nitration of 2,4,6-Trinitrobiphenyl.—Because of uncertainty regarding the orienting influence of the picryl group in electrophilic aromatic substitution, and as a first step in a possible assessment of the relative importance of the influences pictured in Charts III and IV, we have studied the nitration of 2,4,6-trinitrobiphenyl. In connection with this study, the three expected mononitration products, namely, 2,2′,4,6-, 2,3′,4,6-, and 2,4,4′,6-tetranitrobiphenyl, were synthesized by Ullmann reactions[9] between picryl chloride and the appropriate iodonitrobenzene in order to have standards for use in analysis of the reaction product.

Nitration of 2,4,6-trinitrobiphenyl was carried out with an excess of nitric acid in acetic acid in a boiling water bath for 2 hr. By pouring the reaction mixture into water, the product was obtained in quantitative yield. In separate experiments, each of the three expected mononitration products was treated similarly and was recovered almost quantitatively, unchanged in melting point and appearance.

By fractional crystallization of the nitration product, 2,4,4′,6-tetranitrobiphenyl (para substitution product) was isolated in crude form in about 30% yield and in pure form in 15% yield. Despite several changes of solvent, however, fractional crystallization did not yield another pure isomer.

Attempts to separate or to analyze the nitration mixture by thin layer and column chromatography were unsuccessful. The mass spectra of the three isomers were obtained but were too complex and too poorly reproducible to be of value in quantitative analysis of the mixture. The infrared spectra of the three isomers were simple, and the differences among them appeared to be too small to make them useful for quantitative analysis. Ultraviolet absorption spectroscopy appeared unpromising as a method of analysis, in view of its proven inadequacy with the nitroethylbenzenes.[10] The nmr spectra of the three isomers, however, presented in part in Chart IV, showed significant marked differences and seemed to offer a means of quantitative analysis of the nitration mixture.

Nmr Analysis.—The nmr spectra of the nitration product and of the three isomeric tetranitrobiphenyls (or nitropicrylbenzenes) were obtained in dimethyl sulfoxide (DMSO) as solvent. The solvent signal provided a convenient upfield reference point. Integrator tracings were run in the aromatic region, 410–290 cps downfield from the DMSO singlet.

All samples showed an isolated singlet displaced about 402 cps from the DMSO singlet, which accounted for precisely one-third of the total radiant energy absorption in the aromatic region.[11] Clearly, this singlet arose from the two isolated protons on the triply nitrated ring.

The remaining two-thirds of the absorption occurred almost wholly in the region 290–360 cps downfield from the DMSO singlet. This part of the spectrum for each isomer and the nitration product is shown in Figure 1.

The integrator curves in this region were converted to digital form and normalized. Base lines and upper limits (horizontal portions of the integrator tracings) were carefully selected, with attention being paid to mutual alignment of the several curves both horizontally and vertically. The height of each curve above the base line was measured at integral values of the chemical shift with respect to the DMSO singlet.[12]

---

(6) Steric hindrance, of course, would be expected to reduce the amount of ortho substitution. A pathway favoring ortho substitution, involving an initial association of the nitrating agent with the nitro groups, followed by an intramolecular rearrangement, cannot be ruled out however (ref 5, p 76).

(7) Reference 5, footnote, p 163.

(8) F. Swarts, *Bull. Acad. Roy. Belg.* 389 (1920); *Chem. Abstr.*, **16**, 2316 (1922).

(9) F. Ullmann and J. Bielecke, *Ber.*, **34**, 2174 (1901).

(10) L. Fey and J. Rusu, *Rev. Roum. Chim.*, **14**, 613 (1969); *Anal. Abstr.*, **19**, 1410 (1970).

(11) The spectra were run several times and with different samples, and the position of this singlet for the ortho isomer was always found to be about 1 cps further downfield than that for the other isomers and the nitration mixture, showing greater deshielding by the proximal nitro group.

(12) An illuminated magnifier having a millimeter scale at the field of vision was used, of a type used by philatelists and like the "Flash-O-Lens" magnifiers available from most laboratory supply houses.

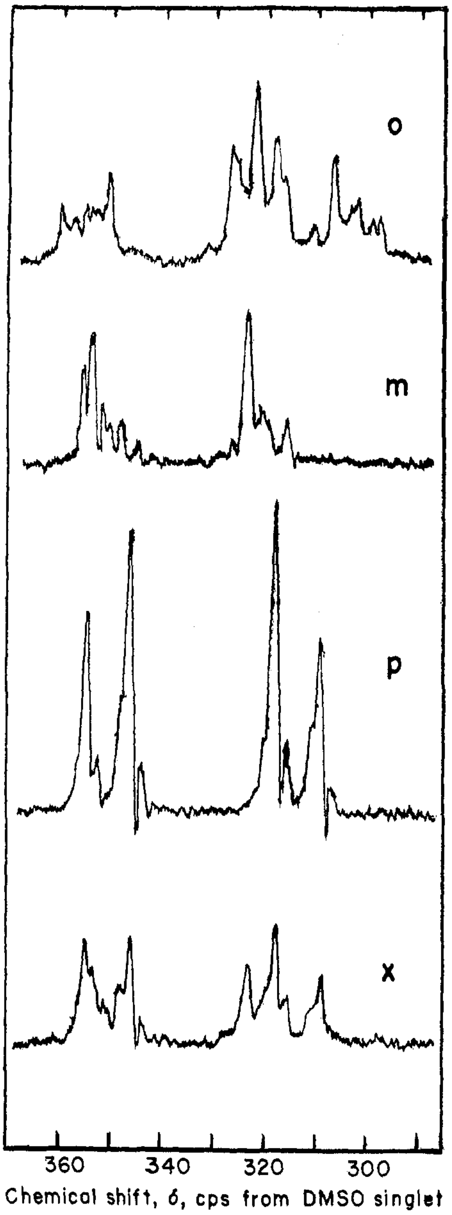


Figure 1.—Portions of the proton nmr spectra of *o*-, *m*-, and *p*-nitropicrylbenzene and of the product (x) of nitration of 2,4,6-trinitrobiphenyl.

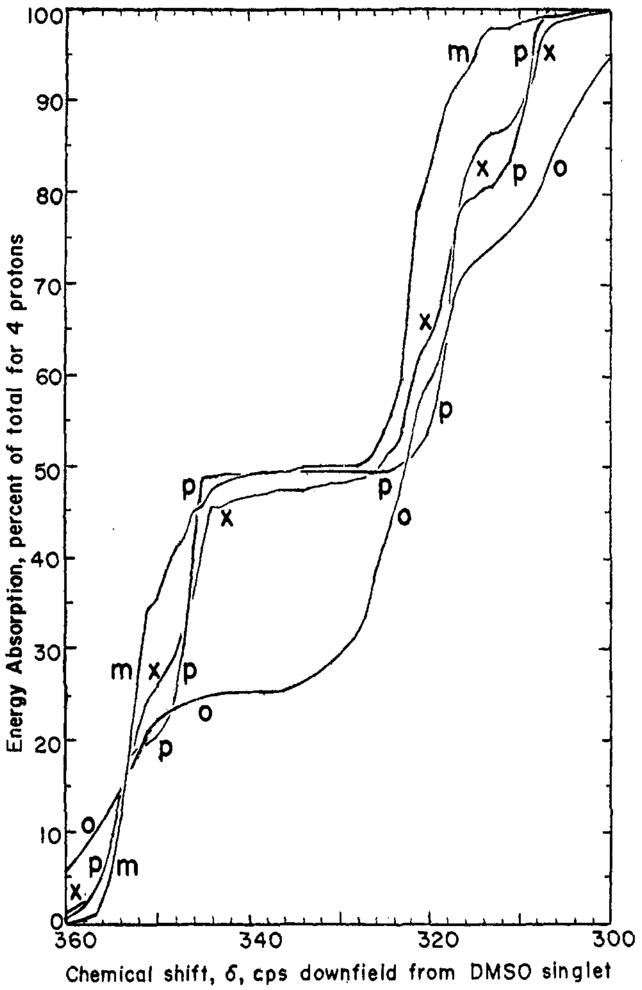


Figure 2.—Normalized A-60 nmr spectrophotometer integrator curves for four protons of *o*-, *m*-, and *p*-nitropicrylbenzene and of the product (x) of nitration of 2,4,6-trinitrobiphenyl.

Each height was converted to a percentage of the total absorption for the four protons involved. Typical normalized integrator curves are presented in Figure 2.

The curve for the nitration product, labeled "x," clearly shows the presence of the ortho isomer, especially in the region around 340 cps where the ortho curve has a plateau at 25% and the meta and para curves are nearly coincident at about 50% of the total absorption. An estimate of the percentage of ortho isomer could readily be made by using the data at several integral values of the chemical shift in this region. With this estimate of the ortho percentage, the percentages of meta and para isomers could be estimated by using the data in the regions around 350 and 320 cps, where the meta and para curves differ widely.

One set of data thus gave the result 8.2 ± 1.0% ortho, 25.0 ± 5.0% meta, and 66.8 ± 5.0% para. Another set of data obtained on a different day with different samples gave the result 8.4 ± 1.2% ortho, 26.0 ± 5.0% meta, and 65.6 ± 5.0% para. It did not seem to be possible to reduce the uncertainty in the meta and para percentages below 5% by using the data in this way.

Accordingly, synthetic mixtures of the three isomers were prepared having nearly the composition indicated by the above treatment of the data. Integrator curves for two such mixtures that seem to bracket the nitration product mixture are shown in Table I. They are designated "W" and "Y," while the nitration product is "X."[13] The differences, Y − X, are mostly smaller than the differences W − X, and a statistical treatment based on 20 points (those designated by footnote *f*), for which the difference between W and Y is large, led to the result that the difference between X and Y is 41 ± 12% of the difference between W and Y. Interpolating to this extent between the compositions of the mixtures W and Y gives a mixture "Z" that is 8.0 ± 0.4% ortho, 30.0 ± 0.8% meta, and 62.0 ± 0.8% para. The uncertainty in the meta and para percentages is taken as 12% of the difference (6.8) in the percentages of meta isomer in the mixtures W and Y, while the uncertainty in the ortho percentage is made conservatively so as to include both synthetic mixtures and in recognition of the fact that it was not possible to reproduce an in-

---

[13] The product curve "X" in Table I is an average of two curves obtained on different days. After alignment of the two sets of data so as to make the algebraic sum of the differences between them equal to zero, the average of the differences between the 68 points for each curve was 0.39.

Table I

Comparison of Normalized Integrator Curves

δ,[a] cps	Diff W − X	Syn mix[b] W	Product[c] X	Syn mix[d] Y	Diff Y − X	Calcd diff[e] Z − X
365	0.4	0.4	0.0	0.0	0.0	0.2
4	0.2	0.4	0.2	0.2	0.0	0.1
3	0.0	0.4	0.4	0.4	0.0	0.0
2	0.0	0.6	0.6	0.6	0.0	0.0
1	−0.1	0.8	0.9	0.8	−0.1	−0.1
360	−0.2	0.9	1.1	1.0	−0.1	−0.1
9	−0.7	1.2	1.9	1.6	−0.3	−0.5
8	−0.5	1.7	2.2	2.2	0.0	−0.2
7	−0.5	2.3	2.8	3.2	0.4	0.0
6	−0.4	4.0	4.4	5.1	0.7	0.3
5	−0.2	7.2	7.4	8.2	0.8	0.4
4	0.3	12.3	12.0	13.6	1.6	1.1
3	−0.6	17.1	17.7	18.8	1.1[f]	0.4
2	−1.1	20.4	21.5	22.4	0.9[f]	0.1
1	−1.6	22.9	24.5	24.8	0.3[f]	−0.5
350	−1.4	24.5	25.9	26.5	0.6[f]	−0.2
9	−1.6	26.1	27.7	28.3	0.6[f]	−0.3
8	−0.8	28.4	29.2	29.6	0.4[f]	−0.1
7	−1.9	30.3	32.2	32.8	0.6[f]	−0.4
6	−0.9	35.3	36.2	37.2	1.0[f]	0.2
5	−0.7	40.4	41.1	42.0	0.9[f]	0.3
4	0.4	45.8	45.4	46.0	0.6	0.5
3	0.8	46.3	45.5	46.2	0.7	0.7
2	0.4	46.6	46.2	46.9	0.7	0.6
1	0.3	46.8	46.5	47.1	0.6	0.5
340	0.3	47.2	46.9	47.2	0.3	0.3
9	0.2	47.2	47.0	47.2	0.2	0.2
8	0.0	47.2	47.2	47.4	0.2	0.1
7	−0.1	47.3	47.4	47.4	0.0	0.0
6	−0.3	47.3	47.6	47.6	0.0	−0.1
5	−0.2	47.4	47.6	47.8	0.2	0.0
4	−0.2	47.4	47.6	47.9	0.3	0.1
3	−0.4	47.4	47.8	48.1	0.3	0.0
2	−0.3	47.6	47.9	48.2	0.3	0.0
1	−0.3	47.8	48.1	48.2	0.1	−0.1
330	−0.2	48.0	48.2	48.3	0.1	0.0
9	−0.3	48.2	48.5	48.6	0.1	−0.1
8	−0.2	48.5	48.7	49.0	0.3	0.1
7	−0.2	49.0	49.2	49.5	0.3	0.1
6	−0.2	49.7	49.9	50.4	0.5	0.2
5	−0.6	50.5	51.1	51.6	0.5	0.1
4	−0.6	51.4	52.0	52.8	0.8[f]	0.2
3	−1.0	52.8	53.8	54.7	0.9[f]	0.1
2	−1.9	55.5	57.4	58.4	1.0[f]	−0.2
1	−2.5	59.3	61.8	62.4	0.6[f]	−0.6
320	−2.5	61.5	64.0	64.3	0.3	−0.9
9	−3.2	63.5	66.7	66.8	0.1	−1.2
8	−3.1	67.7	70.8	70.6	−0.2	−2.0
7	−3.4	72.2	75.6	75.6	0.0	−1.4
6	−2.3	79.1	81.4	82.6	1.2[f]	−0.2
5	−1.2	82.1	83.3	84.8	1.5[f]	0.4
4	−2.4	83.1	85.5	86.8	1.3[f]	−0.2
3	−1.5	84.9	86.4	87.4	1.0[f]	0.0
2	−1.5	85.3	86.8	87.9	1.1[f]	0.0
1	−1.0	86.3	87.3	88.5	1.2[f]	0.3
310	−1.4	87.5	88.9	90.1	1.2[f]	0.1
9	−0.7	90.3	91.0	92.4	1.4	0.6
8	0.0	93.9	93.9	95.6	1.7	1.0
7	0.2	97.8	97.6	98.3	0.7	0.5
6	0.3	98.7	98.4	98.7	0.3	0.3
5	0.5	99.3	98.8	99.1	0.3	0.4
4	0.6	99.7	99.1	99.4	0.3	0.4
3	0.5	99.8	99.3	99.5	0.2	0.3
2	0.4	99.9	99.5	99.6	0.1	0.2
1	0.2	99.9	99.7	99.7	0.0	0.1
300	0.3	100.1	99.9	99.9	0.0	0.1
9	0.2	100.1	99.9	99.9	0.0	0.1
8	0.5	100.5	100.0	100.0	0.0	0.2
					Algebraic sum	2.5
					Average $\lvert Z - X \rvert$	0.31

[a] Chemical shift downfield from DMSO singlet. [b] Synthetic mixture: 8.4% *o*-, 25.9% *m*-, and 65.7% *p*-nitropicrylbenzene. [c] Product of nitration of picrylbenzene (2,4,6-trinitrobiphenyl). [d] Synthetic mixture: 7.8% *o*-, 32.7% *m*-, and 59.5% *p*-nitropicrylbenzene. [e] Differences between product curve X and a curve Z, calculated by interpolation between curves W and Y, for a mixture: 8.0% *o*-, 30.0% *m*-, and 62.0% *p*-nitropicrylbenzene. [f] These points were used in estimation of the composition of X (see text).

tegrator curve with an average deviation for 68 points of less than about 0.4 percentage units.[13]

An integrator curve Z could be calculated, then, for a mixture that is 8.0% *o*-, 30.0% *m*-, and 62.0% *p*-nitropicrylbenzene. The differences between that curve and the curve X for the nitration product are tabulated. Their average is 0.31 percentage units and their algebraic sum is nearly zero (Table I).

It is concluded, therefore, that the nitration of 2,4,6-trinitrobiphenyl gives a mixture that is very nearly 8.0% *o*-, 30.0% *m*-, and 62.0% *p*-nitropicrylbenzene. The $^1/_2$ meta/para ratio, 0.24, leads to classification of the picryl group as an ortho-para-directing substituent, while the very low $^1/_2$ ortho/para ratio, 0.065 indicates much steric hindrance to substitution in an ortho position.

Experimental Section

Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Picryl chloride was prepared by the reaction of pyridine picrate with phosphorus oxychloride according to published procedures,[14] mp 78–81° (lit.[14] 79–81°).

Iodobenzene was prepared by iodination of benzene in the presence of nitric acid,[15] bp 184–186° (lit.[15] 184–186°).

o-, *m*-, **and** *p*-**Iodonitrobenzene** were prepared by diazotization of the corresponding nitroaniline and addition of the filtered diazonium salt solution to a 25% solution of potassium iodide in water.[16] The *p*-iodonitrobenzene solidified and was collected by filtration with suction and purified by crystallization from 95% ethanol. The *o*- and *m*-iodonitrobenzene separated as oils and were purified by distillation with steam: ortho, mp 52–54° (lit.[17] 54°); meta, mp 37–38° (lit.[17] 38.5°); para, mp 171–173° (lit.[17] 174°).

2,4,6-Trinitrobiphenyl was prepared by an Ullmann reaction between picryl chloride and iodobenzene[3a] (for procedure, see below). It crystallized from 95% ethanol as golden brown leaflets, mp 128–130° (lit.[3a] mp 130°).

o-, *m*-, **and** *p*-**Nitropicrylbenzene** were prepared by Ullmann reactions between picryl chloride and the corresponding iodonitrobenzene. Several different procedures were used in efforts to maximize yields. The copper bronze was described as "Palegold Extra Brilliant No. 7," manufactured by U. S. Bronze Powders, Inc., Flemington, N. J. It was used with and without activation with iodine in acetone.[18] A typical procedure was as

---

[14] R. Boyer, E. Y. Spencer, and G. F. Wright, *Can. J. Res., Sect. B*, **24**, 200 (1946).

[15] F. B. Dains and R. Q. Brewster in "Organic Syntheses," Collect Vol. I, 2nd ed, A. H. Blatt, Ed., Wiley, New York, N. Y., 1941, p 323.

[16] A. I. Vogel, "A Textbook of Practial Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 600.

[17] I. Heilbron, Ed., "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965, pp 1871–1872.

[18] Reference 16, p 192.

follows. In a 125-ml erlenmeyer flask were placed 0.5 g of picryl chloride, 0.5 g of *o*-iodonitrobenzene, and 0.5 ml of dimethylformamide (DMF). The solids were brought into solution by slight heating and mixed thoroughly by swirling, and 0.45 g of copper bronze (untreated) was added and mixed in thoroughly by swirling. The brilliant golden fluid mixture was heated at 160° (oil bath) for 30 min, whereupon it became dull brown and lost its fluidity. It was cooled slightly, 10 ml of 95% ethanol was added, and the mixture was boiled for several minutes with stirring with a glass rod and then filtered. This extraction with hot ethanol was repeated twice. The combined filtrates were treated with decolorizing carbon and filtered. Upon cooling, the filtrate deposited crystals. The solvent was removed by decantation; the crystals were washed with 95% ethanol and recrystallized from 95% ethanol, yield 75 mg (11%), golden yellow prisms, mp 172–173°. When the mother liquor from recrystallization of the product from a previous run was used for the recrystallization, the yield was 106 mg (16%). The reaction was also carried out without DMF with similar results.

In variations of the foregoing procedure, reactions were carried out successfully with as much as 10 g of each halide in as much as 100 ml of DMF with reflux times of 7–8 hr and also without DMF at temperatures as high as 190°. In some large-scale runs without DMF, however, and at the higher temperatures, violent decomposition occurred. The compounds are described in Table II.

TABLE II

NITROPICRYLBENZENES

	Isomer		
	Ortho	Meta	Para
Appearance	Golden yellow prisms	Yellow microneedles	Tan microcrystalline powder
Mp, °C	172–173	181–184	200–202
Solvent for crystn	95% EtOH	95% EtOH	Aqueous HOAc
Anal. Found:[a]			
C, %	43.29	43.19	43.34
H, %	1.77	1.96	1.80
N, %	14.74	14.68	15.38

[a] *Anal.* Calcd for $C_{12}H_6N_4O_8$: C, 43.11; H, 1.80; N, 16.76.

Nitration of 2,4,6-Trinitrobiphenyl.—A mixture of 10 g of 2,4,6-trinitrobiphenyl, 100 ml of glacial acetic acid, and 100 ml of 90% ("fuming") nitric acid (density 1.5), contained in a 500-ml erlenmeyer flask, was warmed to bring the solid into solution, mixed thoroughly by swirling, and placed in a boiling water bath for 2 hr. The mixture was poured with stirring into an ice–water mixture. The precipitated solid was collected by filtration with suction, washed thoroughly with ice-cold water, and air-dried to yield 12 g of tan microcrystalline powder (theory 11.6 g).

The nitration product (10 g) was boiled with ethanol and separated into "alcohol-soluble" and "alcohol-insoluble" fractions. The alcoholic extract yielded a yellow solid, mp 136–146°, which after several recrystallizations from 1:1 methanol–ethanol gave 3 g (30%) of solid, mp 152–153°. The melting point was depressed to 129–131° by mixing with *o*-nitropicrylbenzene but was not depressed when mixed with *m*-nitropicrylbenzene. This was thought to be a crude or polymorphic form of *m*-nitropicrylbenzene, but its nmr spectrum showed that it contained all three isomers in about the same proportions as the crude nitration mixture. Recrystallization from several solvents did not effect further purification. The "alcohol-insoluble" fraction (3 g, mp 175–185°) was recrystallized from 3:1 methanol–ethanol and gave 1.5 g (15%) of pure *p*-nitropicrylbenzene, identified by its nmr spectrum and its mp 199–200°, undepressed when mixed with authentic material.

Tests of Stability of Product Isomers.—About 150 mg of each of the isomeric nitropicrylbenzenes was dissolved in a mixture of glacial acetic acid and concentrated nitric acid taken in the same proportions as for the nitration (10 ml of each per gram of solid). The mixtures, contained in 18 × 150 mm test tubes, were heated in a boiling water bath for 2 hr. Distilled water was added dropwise to the hot solutions to the point of incipient crystallization. The mixtures were allowed to cool thoroughly. The crystalline material in each test tube was collected by filtration with suction, washed thoroughly with cold water, and dried in an oven at 80°. Weights, melting points, and nmr spectra were obtained.

Details are presented in Table III. The nmr spectra of the recovered materials were the same as those of the starting materials. There was no evidence of nitration, and the small losses are attributable to solubility in the media.

TABLE III

TESTS OF STABILITY OF NITROPICRYLBENZENES TO NITRATING CONDITIONS

	Isomer		
	Ortho	Meta	Para
Initial wt, mg	171.5	157.4	146.6
Initial mp, °C	172–173	181–184	200–202
Recovered wt, mg	154.4	141.4	122.2 (141.0)[a]
Recovered, %	90	90	83 (96)[a]
Recovered mp, °C	172–173	181–184	200–202

[a] Including a second crop, mp 199–202°, recovered from the filtrate after dilution with water.

Nmr spectra were obtained with a Varian A-60 nmr spectrophotometer. Solids were dried in a vacuum (oil pump) at 100° (boiling water bath) before preparation of the solutions. The dimethyl sulfoxide (DMSO) used as solvent was scanned at high amplification and was found to be free of absorption in the aromatic region. About 100 mg of each solid was dissolved in about 0.5 ml of DMSO. The solutions were estimated to be about 20% by weight and about 0.5 *M*. Special care was taken to eliminate pen drift during integration by balancing of the detector zero and detector phase circuits. For additional details, see text.

Registry No.—**1**, 29128-23-2; *o*-nitropicrylbenzene, 24322-55-2; *m*-nitropicrylbenzene, 24322-58-5; *p*-nitropicrylbenzene, 24322-57-4.