Synthesis of 2,4,7-Trinitro-9-fluorenol and Some Related Compounds. Selective Reduction of Polynitroaromatic Carbonyl Compounds[1,2]

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2,4,7-Trinitrofluorenone (I) has been selectively reduced to 2,4,7-trinitro-9-fluorenol (IV) through 2,4,7-trinitrofluorenone hydrazone (II) and 9-diazo-2,4,7-trinitrofluorene (III). The sequence appears to provide a method of general utility for selective reduction of a carbonyl group in polynitroaromatic carbonyl compounds. Compound III was converted directly to 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate, acetate, and formate (V, VI, and VII, respectively) and 9-bromo-2,4,7-trinitrofluorene (VIII). Several crystalline molecular complexes involving V and VI as acceptors were prepared.

As part of a study of charge-transfer complexes in solvolysis reactions,[1] synthesis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (V) and 9-bromo-2,4,7-trinitrofluorene (VIII) was undertaken. In addition to their interest in the study of the chemical behavior of charge-transfer complexes, 9-substituted 2,4,7-trinitrofluorenes are of interest as reagents of potential use in the resolution of polycyclic aromatic hydrocarbons through complex formation.[3]

The most direct approach to 2,4,7-trinitro-9-fluorenol and its derivatives appeared to be selective reduction of the known[4] 2,4,7-trinitrofluorenone. It has been reported that selective reduction of a carbonyl group in the presence of an aromatic nitro group can be effected by aluminum isopropoxide,[5] sodium borohydride,[6] a mixture of sodium borohydride and aluminum chloride,[7] and a mixture of lithium aluminum hydride and aluminum chloride.[8] Though Arcus and Coombs[9] successfully reduced 2-nitrofluorenone and 3-nitrofluorenone to 2-nitro-9-fluorenol and 3-nitro-9-fluorenol, respectively, using aluminum isopropoxide, Pan and Fletcher[10] obtained only an unidentified high-melting material from an attempted reduction of 2-nitrofluorenone using sodium borohydride. Similarly, Newman and Lutz[3,11] were unable to reduce 2,4,7-trinitrofluorenone to 2,4,7-trinitro-9-fluorenol with sodium borohydride "or by any other method."[3] In the present work, attempts to obtain the alcohol IV by direct reduction of I using sodium borohydride, sodium borohydride–aluminum chloride, or lithium aluminum hydride–aluminum chloride were unsuccessful. In all cases, insoluble, high-melting materials which resisted purification were obtained. Similarly, attempted reduction with aluminum isopropoxide or monochloroaluminum isopropoxide[12] met with failure. In addition, several unsuccessful attempts were made to reduce I to 9-amino-2,4,7-trinitrofluorene by the Leuckart method and to 2,4,7-trinitrofluorene by the Wolff-Kishner method. It soon became apparent that any method involving basic conditions led to highly colored materials from which neither pure starting material nor any identifiable product could be obtained.

The desired 2,4,7-trinitro-9-fluorenol was finally obtained *via* a synthetic route parallel to that reported by Staudinger and co-workers[13,14] for conversion of fluorenone to fluorenol. The method is outlined in Figure 1. Trinitrofluorenone (I) was converted to its hydrazone (II) by treatment with hydrazine hydrate in glacial acetic acid. Attempts to oxidize the hydrazone II to 9-diazo-2,4,7-trinitrofluorene (III) using yellow mercuric oxide were unsuccessful. Schroeder and Katz[15] have reported the use of silver oxide as a more superior oxidizing agent in the preparation of diaryldiazomethanes. Using equivalent amounts of silver oxide in tetrahydrofuran, III was obtained in good yields after five hours of refluxing. 2,4,7-Trinitro-9-fluorenol (IV) was obtained by hydrolysis of III in aqueous nitromethane using fluoboric acid as a catalyst. The use of hydrochloric and sulfuric acids for this purpose failed, presumably because of competing nucleophilic attack by the chloride or bisulfate ion to give 2,4,7-trinitro-9-fluorenyl chloride or 2,4,7-trinitro-9-fluorenyl hydrogen sulfate. On the other hand, the nonnucleophilic fluoborate ion permits exclusive nucleophilic attack by water. Oxidation of IV using sodium dichromate in glacial acetic acid led

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[1] Presented in part before the Division of Organic Chemistry, 139th Meeting of the American Chemical Society, St. Louis, Mo. March 22, 1960. (Abstracts, p. 22-O)

[2] Abstracted from a thesis submitted by Samuel S. Wang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1961.

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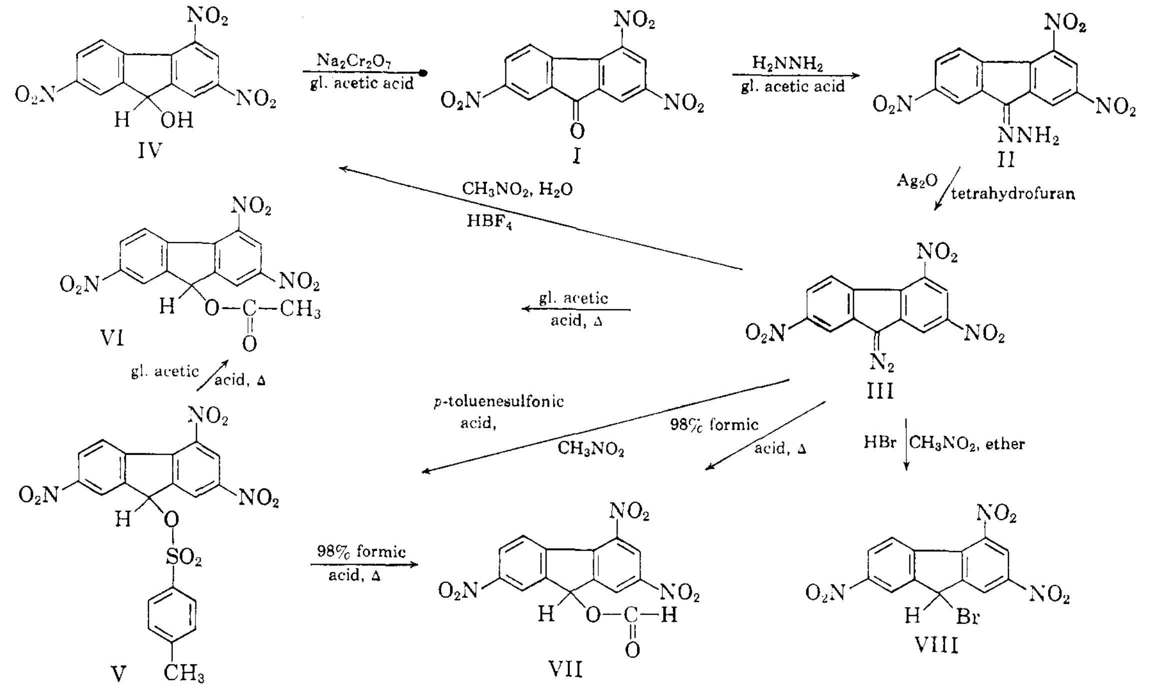

Figure 1

to a material of melting point 173–174°, having an infrared spectrum identical to that of 2,4,7-trinitrofluorenone. A mixed melting point with authentic 2,4,7-trinitrofluorenone showed no depression. The acetate VI and formate VII were obtained directly from III by heating in glacial acetic acid and 98% formic acid, respectively. These compounds were also obtained by similar treatment of the *p*-toluenesulfonate V which was obtained by treatment of III with *p*-toluenesulfonic acid in nitromethane solution. Treatment of III with 48% aqueous hydrogen bromide in a nitromethane–ether mixed solvent led to the bromide VIII.

Table I summarizes the analytical and infrared spectral evidence upon which the structures of compounds II to VIII are based. In the infrared spectra of compounds I to VIII, inclusive, the aromatic nitro groups were indicated by a strong band or pair of bands in the region 6.40 to 6.60 μ and a strong band between 7.42 and 7.56 μ.[16] Bands at 8.36 μ (m) and 5.74 μ (s) in the spectrum of I, due to the carbonyl group, were absent in the spectra of II, III, IV, and VIII.

In conclusion, the sequence of reactions I → II → III → IV appears to provide a useful method for selective reduction of a carbonyl group in a polynitroaromatic carbonyl compound or in other base-sensitive carbonyl compounds.

The formation of crystalline molecular complexes involving aromatic donors and 2,4,7-trinitrofluorenone is well known.[17] The complex forming properties of V and VI were investigated briefly in the present work. Both compounds showed much less tendency to form crystalline molecular complexes than 2,4,7-trinitrofluorenone. The crystalline molecular complexes are described in Table II.

Experimental[18]

2,4,7-Trinitrofluorenone (I) was prepared by the method of Woolfolk and Orchin,[4] m.p. 173–175° (reported,[4] m.p. 175.2–176°, corr.).

2,4,7-Trinitrofluorenone Hydrazone (II).—A solution of 63 g. (0.2 mole) of 2,4,7-trinitrofluorenone in 500 ml. of glacial acetic acid was maintained at 80–85° on a steam cone while a solution prepared by carefully mixing 20 ml. of 100% hydrazine hydrate and 50 ml. of glacial acetic acid was introduced with vigorous stirring. The solution turned deep red and then to a thick orange paste. The mixture was heated for an additional 30 min. and then suction filtered. The crude product was washed several times with water and with 95% ethyl alcohol and air-dried overnight. After further drying on a steam cone in a porcelain dish for several hours the acetic acid-free product weighed 61.5 g. (92.5%) and melted at 242–245° with decomposition. A small amount of the dried product was recrystallized from nitromethane (1 g. in 150 ml.) and washed with ether. The purified material melted at 250–252°.

Anal. Calcd. for $C_{13}H_7N_5O_6$: C, 47.45; H, 2.12; N, 21.25. Found: C, 47.30; H, 2.47; N, 21.20.

Infrared spectrum of II: 2.96 (w), 3.02 (w), 3.10 (w), 6.24 (w), 6.46–6.62 (split, s), 7.44 (s), 7.56 (m), 8.30 (w), 9.22 (w), 9.34 (w), 10.76 (w), 11.23 (broad, w), 11.40 (w), 11.84–11.94 (split, m), 13.74 (m), 14.14 (w).

9-Diazo-2,4,7-trinitrofluorene (III).—In a three-neck flask equipped with an efficient power driven stirrer and a

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[17] (a) M. Orchin, L. Reggel, and E. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946); (b) M. Orchin, L. Reggel, and E. O. Woolfolk, *J. Am. Chem. Soc.*, **69**, 1225 (1947).

[18] All melting points are uncorrected. Microanalyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England. Infrared spectra were taken in Nujol mull using a Perkin-Elmer Model 21 spectrophotometer.

TABLE I

SUMMARY OF ANALYTICAL AND SPECTRAL DATA FOR DERIVATIVES OF 2,4,7-TRINITROFLUORENE

Compound	M.P.	Analytical Data				Infrared Data	
			C	H	N	Found	Assignment
II	250–242	Calcd.	47.45	2.12	21.25	2.96 μ (w)	
		Found	47.30	2.47	21.10	3.02 μ (w)	N—H stretching[a]
						3.10 μ (w)	
III	204–205	Calcd.	47.70	1.53	21.40	4.78 μ (s)	N=N stretching, diazo group[b]
		Found	47.73	1.72	21.40		
IV	172–174	Calcd.	49.22	2.22	13.25	2.85 μ (m)	O—H stretching[c]
		Found	49.08	2.32	12.86		
					12.90		
V	208–210	Calcd.	50.96	2.78	8.91	7.28 μ (s)	
		Found	51.06	2.97	8.80	8.42 μ (m)	Sulfonate ester group[d]
						8.51 μ (s)	
VI	240–242	Calcd.	50.15	2.52	11.70	5.74 μ (s)	C=O stretching[e]
		Found	50.02	2.57	11.78	8.26 μ (s)	Acyl C—O stretching[f]
						9.55 μ (m)	Alkyl C—O stretching[f]
VII	234 dec.	Calcd.	48.71	2.04	12.17	5.76 μ (s)	C=O stretching[e]
		Found	48.71	1.66	11.99	8.78–8.86 μ	C—O stretching[f]
			49.10	2.16	12.28	(split, s)	
VIII	179–180	Calcd.	41.07	1.59	11.06		
		Found	41.42	1.86	11.36		

[a] Ref. 16, p. 249. [b] P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Am. Chem. Soc.*, 79, 5756 (1957). [c] Ref. 16, p. 96. [d] Ref. 16, p. 364. [e] Ref. 16, p. 179. [f] Ref. 16, p. 188.

TABLE II

COMPLEXES OF AROMATIC HYDROCARBONS WITH 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE AND 2,4,7-TRINITRO-9-FLUORENYL ACETATE

	Acceptor					
		V			VI	
Donor	M.P.	Color	Analysis, % N	M.P.	Color	Analysis, % N
Acenaphthene				190	Orange	Calcd. 8.19 Found 8.30
Fluoranthene	163–165	Yellow	Calcd. 6.24 Found 6.40	160–163	Yellow	Calcd. 7.48 Found 7.48
Pyrene	138	Red	Calcd. 6.24 Found 6.21	195–197	Orange	Calcd. 7.48 Found 7.55
Phenanthrene	160–162	Yellow	Calcd. 6.47 Found 6.46			

condenser, 24.7 g. (0.075 mole) of dried crude hydrazone II was suspended in 2300 ml. of technical tetrahydrofuran. The mixture became homogeneous after stirring at reflux after which 19 g. (0.082 mole) of powdered silver oxide was introduced in small portions over a period of 20 min. Refluxing was continued for 5 hr. with vigorous stirring. The silver metal residue was filtered off by gravity while the solution was still warm, and washed with two 50-ml. portions of tetrahydrofuran. The filtrate was concentrated to about 100 ml. in a solvent evaporator under reduced pressure and gentle heat. As solid precipitated, the evaporation was interrupted several times and the crude product filtered off. The combined orange-yellow material was washed with ether and dried; yield 21 g. (89%), m.p. 203–204° dec. Further purification was achieved by crystallizing the product from 1600 ml. of nitromethane. The purified product (fine orange needles) was filtered and washed with ether. The dried product weighed 18 g. (73%) and melted at 204–205°.

Anal. Calcd. for $C_{13}H_5N_5O_6$: C, 47.70; H, 1.53; N, 21.40. Found: C, 47.73; H, 1.72; N, 21.40.

Infrared spectrum of III: 4.78 (s), 6.36 (w), 6.51–6.60 (split, m), 7.04 (s), 7.42–7.56 (split, s), 8.18 (w), 9.18 (w), 10.78 (broad, w), 11.26 (w), 12.00 (s), 13.65 (broad, m).

2,4,7-Trinitro-9-fluorenol (IV).—A mixture containing 3.0 g. of III, 50 ml. of nitromethane, 4 ml. of distilled water, and 1.5 ml. of 45% fluoroboric acid was stirred at a temperature of 70–80°. After a short period, evolution of nitrogen ceased and a clear solution was obtained. After an additional 1.5 hr. of stirring at 70–80°, the solution was evaporated to dryness under reduced pressure. The residue was suspended in 50 ml. of ether and stirred for 10 min. The yellow material was filtered off and washed with several 25-ml. portions of hot water. The dried crude product weighed 2.7 g. (93%) and melted at 172–174°. A mixture of this material with 2,4,7-trinitrofluorenone (I) (m.p. 173–175°) melted at 158–160°. Recrystallization from nitromethane–ether left the melting point of IV unchanged.

Anal. Calcd. for $C_{13}H_7N_3O_7$: C, 49.22; H, 2.22; N, 13.25. Found: C, 49.08; H, 2.32; N, 12.86, 12.90.

Infrared spectrum of IV: 2.85 (m), 6.28 (w), 6.58 (m), 7.42 (s), 7.65 (s), 9.24 (m), 9.55 (w), 10.86–11.22 (broad, w), 11.84 (w), 12.16–12.24 (w), 13.62 (m).

Oxidation of 2,4,7-Trinitro-9-fluorenol.—One gram of IV was heated on the steam cone (80–90°) for 4 hr. in 30 ml. of glacial acetic acid containing 1 g. of sodium dichromate dihydrate. Dilution with cold water and filtration yielded a yellow material which melted at 173–174° alone and at 174–175° when mixed with authentic 2,4,7-trinitrofluorenone. Its infrared spectrum was identical to that of I.

2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate (V).—A mixture of 4.0 g. of *p*-toluenesulfonic acid in 80 ml. of nitromethane was heated to 70–80° in a three-neck flask equipped with a condenser and an efficient power driven stirrer. A 6.6-g. (0.02 mole) quantity of III was introduced. Evolution of nitrogen gas ceased in 10–15 min., and a yellow precipitate began to appear. The reaction mixture was stirred at 70–80° for an additional hour. The cooled mixture was allowed to stand in the refrigerator for several hours. After filtering and washing with ether, the dried product melted at 206–208° and weighed 7.5 g. (78%). It was purified by dissolving in 1500 ml. of boiling acetone and concentrating the volume to about 400 ml. on a steam cone. The red-colored solution was filtered and placed in refrigerator for 2 days. The bright yellow crystals were filtered off and washed with ether. The product melted at 208–210°.

Anal. Calcd. for $C_{20}H_{13}N_3O_9S$: C, 50.96; H, 2.78; N, 8.91. Found: C, 51.06; H, 2.97; N, 8.80.

Infrared spectrum of V: 6.26 (m), 6.56 (s), 7.28 (s), 7.46 (s), 7.64 (shoulder), 8.42 (m), 8.51 (s), 9.20 (broad, m), 10.03 (m), 10.48 (m), 10.97 (m), 11.41 (m), 11.72 (s), 11.88 (w), 12.33 (broad, s), 13.08 (m), 13.22 (w), 13.62–13.76 (broad, m), 14.47 (w).

Acetolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate.—A solution containing 2.4 g. of V in 80 ml. of glacial acetic acid was refluxed for 19 hr. On cooling, 1.7 g. (93%) of VI separated. The product melted at 240–242° alone and 241–242° when mixed with authentic VI.

2,4,7-Trinitro-9-fluorenyl Acetate (VI) was prepared by gently refluxing 3.3 g. (0.01 mole) of III in 80 ml. of glacial acetic acid for 2 hr. The solution was cooled to room temperature yielding a light yellow precipitate which was filtered and washed with 95% ethanol. The air-dried product was further dried in a drying oven at 80–90° yielding 3.1 g. (85%) of acetic acid-free product melting at 235° with decomposition. Recrystallization from acetone raised the melting point to 240–242°.

Anal. Calcd. for $C_{15}H_9N_3O_8$: C, 50.15; H, 2.52; N, 11.70. Found: C, 50.02; H, 2.57; N, 11.78.

Infrared spectrum of VI: 5.74 (s), 6.21–6.24 (split, m), 6.55 (s), 7.46 (s), 7.62 (m), 8.16–8.26 (split, s), 9.22 (m), 9.55 (m), 11.00 (w), 11.22 (m), 11.84 (broad, w), 12.04 (w), 12.22 (m), 13.02 (w), 13.37 (s).

Formolysis of 2,4,7-Trinitro-9-fluorenyl *p*-Toluenesulfonate.—Heating 0.5 g. of V in 20 ml. of formic acid (99–100%) for 17 hr. under reflux yielded 0.35 g. (96%) of VII, melting at 232–235°. Mixed melting point with authentic VII was 232–234°.

2,4,7-Trinitro-9-fluorenyl Formate (VII).—A mixture of 3.3 g. (0.01 mole) of III in 50 ml. of formic acid (98–100%) was refluxed for 2 hr. Upon cooling, yellow crystals separated out, which were filtered and washed with alcohol. The dried product melted at 234° dec. and weighed 3.3 g. (95%). Recrystallization from acetone did not raise the melting point.

Anal. Calcd. for $C_{14}H_7N_3O_8$: C, 48.71; H, 2.04; N, 12.17. Found: C, 48.71, 49.10; H, 1.66, 2.16; N, 11.99, 12.28.

Infrared spectrum of VII: 5.76 (s), 6.18 (m), 6.24 (m), 6.50–6.56 (split, s), 7.42 (s), 7.62 (m), 8.36 (m), 8.50 (w), 8.78–8.86 (split, s), 9.12 (m), 9.22 (m), 9.86 (w), 10.28 (w), 10.66 (m), 10.73 (m), 11.10 (s), 11.65 (m), 12.11 (s), 12.80 (w), 12.98 (w), 13.46 (s).

9-Bromo-2,4,7-trinitrofluorene (VIII).—To a mixture of 6.6 g. (0.02 mole) of III in 60 ml. of nitromethane and 150 ml. of diethyl ether, was introduced 35 ml. of aqueous hydrogen bromide (48%). The reaction mixture was refluxed gently for 2.5 hr. with stirring. The cooled solution was filtered and stored in the refrigerator overnight. The yellow crystalline product was collected by suction filtration and washed with small portions of cold ether. Recrystallization of dried material from nitromethane–ether gave 5.4 g. (70.5%) of VII melting at 179–180°.

Anal. Calcd. for $C_{13}H_6N_3O_6Br$: C, 41.07; H, 1.59; N, 11.06. Found: C, 41.42; H, 1.86; N, 11.36.

Infrared spectrum of VIII: 6.20 (w), 6.27 (m), 6.48 (s), 6.59 (s), 7.48 (s), 7.66 (m), 8.43 (w), 8.62 (w), 8.85 (w), 9.20 (m), 10.80 (w), 10.97 (m), 11.10 (w), 11.76 (m), 12.11 (w), 12.28 (s), 12.80 (w), 13.06–13.14 (broad, m), 13.64 (s), 14.18 (w).

Isolation of Crystalline Molecular Complexes.—Approximately equimolar amounts of donor and acceptor compounds were dissolved separately to near saturation in the appropriate solvent at its boiling point. Upon mixing together, deeply colored solutions were obtained. After cooling overnight, the crystalline complexes were collected by filtration, washed with small portions of anhydrous ether, and dried. For complexes of 2,4,7-trinitro-9-fluorenyl acetate, glacial acetic acid solvent was used in all cases. Nitromethane solvent was used in the preparation of all of the 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate complexes with the exception of that with phenanthrene.

The *p*-toluenesulfonate–phenanthrene complex was formed when 500 ml. of hot glacial acetic acid solution of 0.05 g. of the *p*-toluenesulfonate and 5.40 g. of phenanthrene was allowed to stand for several days at room temperature. The bright yellow needles were filtered, washed with small portions of cold acetic acid, and air-dried. The melting points and nitrogen analyses for the six complexes prepared are listed in Table II.

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Multiple Substituent Effects in the Solvolysis and Thiosulfate Reactions of 4-Substituted α-Chloro-3-nitrotoluenes

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The rates of reaction of a series of 4-substituted α-chloro-3-nitrotoluenes with thiosulfate do not fall on the U-shaped curve for the 4-substituted α-chlorotoluenes, but describe a separate U-shaped curve. The rates of solvolysis of both series in 50% ethanol are satisfactorily correlated with σ^+ up to values of 0.2. At more positive values of the substituent constant rates are better correlated with ordinary σ values. The two branches of the solvolysis plot are suggestive of a carbonium ion mechanism and a bimolecular attack of solvent, respectively.

Large deviations from the Hammett equation have generally been recorded[1] for reactions of benzyl halides (3- and 4-substituted α-halotoluenes) with anions.[1,2] Plots of log *k* *vs.* sigma for these reactions are, in general, U- or J-shaped. Similar behavior has been observed in the solvolysis of a series of benzoyl halides.[3] It has been known for

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