oil from which benzoin precipitates upon standing. The last traces of benzoin were obtained by dissolving the oil in a minimum of ether and adding petroleum ether. The mother liquor was concentrated to give a mixture of benzyl alcohol and benzyl benzoate which were analyzed by NMR. The original aqueous layer was acidified with HCl to precipitate the benzoic acid which was filtered, dried, and weighed.

Benzaldehyde plus Potassium Hydride in the Presence of Methyl Iodide. Methyl iodide (8.5 g, 60 mmol) and crown ether (50 mg) were added to washed potassium hydride (4.41 g of dispersion, 33 mmol) in 50 mL of THF. Benzaldehyde (3.2 g, 30 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir at room temperature for 48 h. Workup as usual gave 3.10 g of an oil which analyzed for benzyl alcohol (33%, 10 mmol) and benzyl methyl ether (53%, 16 mmol).

Benzaldehyde plus Potassium Hydride in the Presence of Methyl Benzoate. Methyl benzoate (3.0 g, 22 mmol) and crown ether (50 mg) were added to washed potassium hydride (3.8 g of dispersion, 22 mmol) in 50 mL of THF. Benzaldehyde (2.1 g, 20 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir for 24 h. The usual workup gave benzoin (0.3 g, 1.4 mmol, 14%), benzyl benzoate and methyl benzoate [3.8 g, which analyzed to give 31% (6.1 mmol) and 82% (18 mmol), respectively], and benzoic acid (0.50 g, 4.1 mmol, 21%).

Benzaldehyde plus Sodium Benzyl Oxide. Benzyl alcohol (3.2 g, 30 mmol) was added to washed sodium hydride (1.4 g of dispersion, 33 mmol) in 50 mL of THF. After the sodium hydride had reacted, benzaldehyde (6.6 g, 60 mmol) in 10 mL of THF was added dropwise, and the reaction mixture was allowed to stir for 48 h. Workup as before gave 8.2 g of oil which analyzed for 53% (32 mmol) benzyl alcohol, 33% (21 mmol) benzyl benzoate, and 5% (3 mmol) benzaldehyde. In addition, 1.4 g (12 mmol, 20%) of benzoic acid was isolated.

Benzyl Benzoate plus Potassium Hydride and Crown Ether. Benzyl benzoate (4.3 g, 20 mmol) and crown ether (150 mg) were added to washed potassium hydride (3.8 g of dispersion, 22 mmol) in 50 mL of THF. After 48 h, the reaction mixture was worked up as usual to give 0.64 g (3.0 mmol, 15%) of benzoin, 3.2 g of benzyl benzoate and benzyl alcohol [which analyzed for 50% (10 mmol) and 50% (10 mmol); respectively], and 0.1 g (0.8 mmol, 4%) of benzoic acid.

This procedure was repeated with a larger amount of potassium hydride (7.0 g of dispersion, 40 mmol) to give benzoin (0.95 g, 4.5 mmol, 23%), benzyl benzoate and benzyl alcohol [2.0 g, which analyzed to give 21% (4.1 mmol) and 50% (10 mmol), respectively], and benzoic acid (0.50 g, 4.1 mmol, 21%).

Benzoin Benzoate plus Potassium Hydride and Crown Ether. Benzoin benzoate (3.2 g, 10 mmol)[13] and crown ether (50 mg) were added to washed potassium hydride (1.9 g of dispersion, 11 mmol) in 50 mL of THF. The workup after 24 h at room temperature gave a wet solid from which 1.0 g (3.2 mmol, 32%) of benzoin benzoate was obtained by successive recrystallization with ether/hexane. The mother liquor consisted of benzoin (1.3 mmol, 13%) and deoxybenzoin (3.7 mmol, 37%) plus benzoic acid (0.80 g, 6.6 mmol, 66%).

Benzyl Benzoate plus Potassium Benzyl Oxide and Crown Ether. Potassium (0.86 g, 22 mol) was dissolved in benzyl alcohol (2.2 g, 20 mmol) in 50 mL of THF. The crown ether (100 mg) was added followed by benzyl benzoate (4.3 g, 20 mmol), and the reaction mixture was allowed to stir for 96 h at room temperature. The usual workup gave a mixture of benzyl benzoate and benzyl alcohol (3.5 g, which analyzed for 3.3 mmol (17%) and 2.6 mmol (13%), respectively) plus 2.0 g (16 mmol, 80%) of benzoic acid.

Preparation of Benzyl Mestitoate. Mesitoyl chloride[17] (4.0 g, 22 mmol) was added slowly to a mixture of benzyl alcohol (2.2 g, 20 mmol) and triethylamine (4.0 g, 40 mmol) in 50 mL of toluene, and the reaction mixture was heated to reflux for 12 h. This was cooled, poured into 100 mL of cold water, and extracted with three 50-mL portions of toluene. The combined organic layers were washed twice with 50 mL of saturated, aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated to give a crude solid which was recrystallized from ether/hexane to yield 4.5 g (89%) of the desired ester as white crystals: mp 37–38 °C; NMR ($CDCl_3$, 90 MHz) δ 2.20 (s, 6 H), 2.25 (s, 3 H), 5.20 (s, 2 H), 6.67 (s, 2 H), 7.25 (m, 5 H).

Reaction of Benzyl Mesitoate with Potassium Hydride. A solution of benzyl mesitoate (1.0 g, 4.0 mmol) in 10 mL of THF was added to prewashed potassium hydride (2.0 g of dispersion, 12 mmol) in 25 mL of THF containing 0.52 g (2.0 mmol) of 18-crown-6. The reaction mixture was stirred for 30 min at room temperature and 48 h at 50–60 °C. This was cooled and poured into 50 mL of ice cold 2% HCl and then extracted with three 50-mL portions of ether. The combined organic layers were washed with three 50-mL portions of saturated, aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated to give 0.70 g of a wet solid which was analyzed by NMR integration and comparison with known samples: benzyl alcohol (0.17 g, 1.6 mmol, 40%), 2,4,6-trimethylbenzyl alcohol (0.21 g, 1.4 mmol, 35%), and the mixed α-diketone[18] (0.32 g, 1.3 mmol, 33%). The combined $NaHCO_3$ layers were acidified with dilute HCl to precipitate mesitoic acid which was collected by filtration and allowed to dry to give 0.23 g of product (1.4 mmol, 35%).

Reaction of Benzyl Mesitoate with LDA. LDA (6.0 mmol) was prepared in the usual manner from *n*-BuLi in THF and cooled to -78 °C. A solution of 1.0 g (4.0 mmol) of benzyl mesitoate in 10 mL of THF was added over a 10-min period, and the reaction mixture was allowed to warm to room temperature and stir for a total of 18 h. The same workup as before in potassium hydride reactions gave 1.0 g of a wet solid which was analyzed by NMR integration: benzyl alcohol (0.21 g, 1.9 mmol, 48%), the mixed α-diketone[18] (0.33 g, 1.3 mmol, 33%), and the α-mesitoxy ketone[18] (0.47 g, 1.2 mmol, 30%).

Reaction of Benzyl Benzoate with LDA. LDA (22.0 mmol) was prepared in the usual manner in THF and cooled to -78 °C, and a solution of benzyl benzoate (4.3 g, 20 mmol) in 10 mL of THF was added over a 10-min period. The reaction mixture was allowed to warm to room temperature and, after 18 h of stirring, was worked up as usual to give 4.0 g of crude solid which was analyzed by NMR as benzoin[18] (1.3 g, 6.1 mmol, 31%), benzoin benzoate[18] (1.2 g, 3.8 mmol, 38%), benzyl benzoate (0.9 g, 4.2 mmol, 21%), and benzyl alcohol (0.4 g, 3.7 mmol, 19%).

Another reaction was run in the same way for a total of 48 h at room temperature to give 4.2 g of crude product which analyzed as benzoin[18] (0.53 g, 2.5 mmol, 13%), benzoin benzoate[18] (2.4 g, 7.6 mmol, 76%), benzyl benzoate (1.1 g, 5.0 mmol, 25%), and benzyl alcohol (0.2 g, 1.9 mmol, 10%).

Registry No. Benzaldehyde, 100-52-7; potassium hydride, 7693-26-7; methyl iodide, 74-88-4; methyl benzoate, 93-58-3; sodium benzyl oxide, 20194-18-7; benzyl benzoate, 120-51-4; benzoin benzoate, 1459-20-7; potassium benzyl oxide, 22379-62-0; benzyl mesitoate, 4909-77-7.

(17) Barnes, R. P. "Organic Synthesis"; Wiley, New York 1955; Collect. Vol. III, p 555.

(18) This compound was later isolated as a crystalline solid for unambiguous identification and confirmation of yield.

Selective Nitration of Benzophenone

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Received June 16, 1981

We report the first selective nitration of benzophenone to give *m,m'*-dinitrobenzophenone (93%), a precursor for the corresponding diaminobenzophenone which is of interest in polyimide resins.[1] Most important syntheses of

(1) Bell, V. L. "Abstracts of Papers", Meeting of the American Chemical Society, Division of Organic Coatings and Plastics Chemistry, Dallas, TX, Ap 8, 1973; American Chemical Society: Washington, DC, 1973; p 153.

0022-3263/81/1946-5014$01.25/0

Table I. Nitration of Benzophenone (BZ)[a]

expt	H_2SO_4, wt %	conditions	yield of $BZ(NO_2)_2$, %	% $BZ(NO_2)$	isomer distribution, % (HPLC)				
					o,o'	*o,m'*	*m,m'*	*m,p'*	*p,p'*
1	0[b]		100		7.9	29.7	44.4	17.2	0.8
2	98		100		2.5	20.6	65.2	11.7	0.1
3	98	in CH_2Cl_2	~60[c]	40	9.5	32.6	41.6	13.7	2.6
	oleum (% SO_3)								
4	5.3		99		0.5	19.7	68.6	11.7	0.1
5	12.5		98		1.3	18.5	70.3	9.8	0.1
6	15		96		1.6	17.0	71.5	10.0	0.1
7	18		94			14.7	77.0	8.3	
8	22.5	after 0.5 h (25 °C)	84	5.7		12.1	82.2	5.7	
		upon heating to 70 °C				11.1	82.9	6.0	
		after 0.5 h				5.0	89.1	5.9	
		after 1 h					93.7	6.3	
9	33.0	after 0.4 h (25 °C)		8.0		12.2	81.4	6.4	
		upon heating to 70 °C				6.8	87.5	5.7	
		after 0.2 h	60				93.5	6.5	

[a] 90% HNO_3, 10% excess over stoichiometric amount. [b] 90% HNO_3 solvent. [c] Two-phase system.

m,m'-dinitrobenzophenone are based on nitration of benzophenone, but in selectivities of less than 70%.[2-7] Staedel, for example, nitrated benzophenone with fuming nitric acid in 1894 and isolated three dinitrobenzophenone isomers: *m,m'*, 50%; *o,m'*, 33%; *o,o'*, 17%.[2] In spite of the tedious separation procedure, this reference, to our knowledge, is the only one which reports the distribution of isomers.

Bennett and Grove were interested in the byproducts which accompany the nitration of benzophenone.[5] From the nitration products of benzophenone, either with fuming nitric acid alone or with fuming nitric acid in sulfuric acid, they recovered about 1–3% of a mixture of *m*- and *p*-nitrobenzoic acids. This data, however, lead one to conclude erroneously that the nitro groups are exclusively located in the meta and para positions. This work nevertheless has been quoted to indicate the state of the art even in the most recent literature.[6] The absence of *o*-nitrobenzoic acid among the products of oxidative degradation was assumed to indicate the absence of *o*-nitro substitution. We found, however, that *o*-nitrobenzoic acid is unstable under the reported conditions, and, as will be shown later, the amount of *o*-nitrobenzophenones (*o,m'* and *o,o'*) by direct analysis actually ranges from 19% to 38% under previously reported conditions.

The above indicates that nitration of benzophenone is a nonselective reaction and that the resulting isomers are difficult to separate. When separation succeeds, the yield of *m,m'*-dinitrobenzophenone is only ~40–50%.

Discussion

Synthesis. The six isomers of dinitrobenzophenone in which only one substituent is present on each benzene ring have been synthesized by independent procedures.[1,8] There is very little information in the literature, however, on the distribution of isomers resulting from the nitration of benzophenone.

Our initial attempts to analyze the nitration products of benzophenone by GLC were only partially successful. After much effort, the best that we could do was to analyze isomers by groups rather than individually. This led us to develop an HPLC procedure for analyzing all six dinitrobenzophenones. In practice, the *o,p'*-dinitro isomer was never detected among the nitration products of benzophenone, although it was observed in standards.

Initially, we investigated the nitration of benzophenone in three different systems: 90% nitric acid, 90% nitric acid in the presence of sulfuric acid, and 90% nitric acid in oleum containing up to 15% of sulfur trioxide. In each case an excellent yield of the product was obtained, each product containing five isomers (Table I). The reaction in nitric acid was nonselective, affording only 44% of the *m,m'*-dinitrobenzophenone, which increased to 65% when sulfuric acid was also used. The addition of oleum (5 to 15% SO_3) showed only a small further increase in selectivity to ~70–71%.

A paper on the nitration of benzaldehyde and acetophenone under varying acid conditions by Baker and Moffitt indicates that the largest increase in the *m*-nitro isomer content (~90%) occurs with increasing concentration of sulfuric acid.[9] The use of oleum offers little advantage. Ionization of benzophenone in sulfuric acid afforded a van't Hoff factor *i* of around 2.[10] The values for the *i* factors close to whole numbers indicate that the apparent degree of ionization must be very high. Hence, in the more acidic media, the resonance forms of protonated benzophenone were assumed to become increasingly important during electrophilic reactions.

Although in expt 6 (Table I), for example, the initial oleum contained 15% of sulfur trioxide, calculations showed that when allowance is made for the water of reaction and that present in nitric acid, the sulfur trioxide content at the end of reaction is only ~3%. Calculations also revealed that the highest amount of sulfur trioxide used by Baker and Moffitt is just sufficient to react with

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(3) Barnett, E. B.; Matthews, M. A. *J. Chem. Soc.* **1924**, 125, 767.
(4) Stewart, B. B.; Smith, H. A. *J. Am. Chem. Soc.* **1957**, *79*, 5457.
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(6) "Ullmanns Encyklopadie der Technischen Chemie", 4th ed.; Verlag Chemie: Weinhein/Bergstr., Germany, 1977; Vol. 14, p 224.
(7) David, G. D.; Cook, N. C. U.S. Patent 4 005 102, 1977; CHEMTECH **1977**, 626.
(8) Bell, V. L.; *J. Polym. Sci.* **1976**, *14*, 2275.
(9) Baker, J. W.; Moffitt, W. G. *J. Chem. Soc.* **1931**, 314.
(10) Treffers, H. P.; Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 1708.

Table II. Reaction of Nitro Aromatic Ketones with Oleum[a]

expt	ketone (amt, g)	oleum, g (% SO_3)	temp, °C	time, min	product, g	isomer distribution, % (HPLC) o,o'	o,m'	o,p'	m,m'	m,p'	p,p'	anal.[b]
10	IX (50)	200 (15)	70	30	29.0	7.9	29.7		44.4	17.2	0.8	A
									69.5	30.5	tr	B
11	X (50)	200 (15)	70	60	ND	2.5	20.6		65.2	11.7	tr	A
									85.0	15.0		B
12	XI (30)	600 (5)	90	60	25.5	1.6	17.0		71.3	10.0	0.1	A
							14.7		77.3	8.0		B
13	XII (10)	92 (0)	100	30	9.4		5.0		89.1	5.9		A
							5.0		89.1	5.9		B
14	IX (50)	200 (20)	70	30	ND				67.7	30.0	2.3	B
15	XII (50)	200 (20)	70	60	44.0				93.6	6.4		B
16	XIII (50)	370 (15)	70	60	31.1	0.8	3.0	25.0		13.3	57.9	A
										18.3	81.7	B
17	XIV (50)	370 (15)	70	60	ND	6.1	6.1	31.0		11.3	44.5	A
										19.9	80.1	B
18	XV (10)	100 (20)	70	60	5.1	40.0[c]			60.0[d]		0[e]	A
									100.0[d]			B
19	XVI (6)	57 (20)	70	6	2.7	29.5[c]			62.2[d]		8.3[e]	A
									88.0[d]		12.0[e]	B
20	XVII (10)	100 (20)	25	60	6.7	20.0[c]			70.0[d]		10.0[e]	A
									89.8[d]		10.2[e]	B
21	XVIII (2.6)	45 (10)	50	20	ND	55.0[c]			6.4[d]		38.6[e]	A
									10.5[d]		89.5[e]	B

[a] ND = not determined; IX-XIV, dinitrobenzophenones of different composition; XV, mixture of nitrobenzophenones; XVI, *p*-chloro-*X*-nitrobenzophenones; XVII, mixture of nitroacetophenones; XVIII, nitrobenzils. [b] Analysis of feed, A; analysis of product, B. [c] Ortho. [d] Meta. [e] Para.

the water of reaction. The anhydrous conditions were apparently necessary to minimize the hydrolysis of the intermediate oxonium salt. Thus, it was of interest to determine the effect of even higher acidity on the course of benzophenone nitration. For this purpose, a standard nitration with 90% nitric acid was repeated with oleum containing 33% of sulfur trioxide (expt 9), calculated to give a final sulfur trioxide content of ~12%. Only two isomers were found in our product, *m,m'*- and *m,p'*-dinitrobenzophenones, 93.5% and 6.5%, respectively (60% yield). This run led us to examine systematically the effect of the higher sulfur trioxide content in oleum on the selectivity to the *m,m'*-dinitrobenzophenone by following the course of the nitration at several points of the reaction by HPLC.

The highest selectivity of the *m,m'*-dinitrobenzophenone isomer obtained (~81–82%) was in experiments using 90% nitric acid, oleum containing at least 18% of sulfur trioxide, and mild reaction conditions. This optimum value is believed to be the function of the acidity and is in agreement with the data of Baker and Moffitt (i.e., 0.9 × 0.9 × 100 = 81%). It therefore appears that during dinitration of benzophenone the intermediate mononitrobenzophenone is not completely protonated, except in a high-acidity medium. In this respect, Deno and Schriescheim[11] stated that *m,m'*- and *p,p'*-dinitrobenzhydrols did not appear to be converted appreciably to the corresponding carbenium ions in 97% sulfuric acid, presumably because of the electron-withdrawing effect of the nitro groups.

It was discovered that when the reaction mixture containing isomeric dinitrobenzophenones was heated to 70 °C to finish the nitration, the amount of the *m,m'*-dinitro isomer in the isolated product increased to 93.5%. The increase in the relative amount of *m,m'* isomer, however, occurred at the expense of *o,m'* isomer, which was destroyed.

Heating an isomeric mixture of dinitrobenzophenones in concentrated sulfuric acid (100 °C) had a negligible effect on the isomer distribution (expt 13). In fact, little effect was observed with oleum containing a low percentage of sulfur trioxide (5% SO_3, expt 12, 90 °C). A very pronounced effect, on the other hand, was seen in experiments with oleum containing a high percentage of sulfur trioxide (>15% SO_3, 70 °C), which led to the preferential reaction of *o*-nitrobenzophenones.

To achieve the high *m,m'*-dinitrobenzophenone selectivity of over 90%, the final sulfur trioxide concentration at the end of reaction should be around 10%.

Reaction of Nitro Aromatic Ketones with Oleum. Having discovered a procedure for selectively destroying the *o*-nitro-containing isomers in a mixture of dinitrobenzophenones, we next determined the scope of this novel reaction by treating several nitro aromatic ketones with oleum. In this case, dinitro- and mononitrobenzophenones, chloronitrobenzophenones, nitrobenzils, and nitroacetophenones were used as representative ketones (Table II).

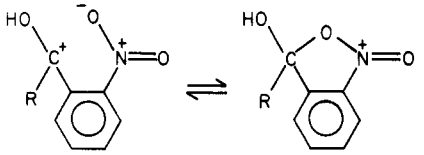
Reactions were carried out by heating the nitro aromatic ketones in oleum, quenching the reaction mixture by pouring it over ice, and either filtering or extracting the mixture with methylene chloride. The experiments were exploratory, and no attempt was made to optimize the reaction parameters. In all of the nitro aromatic ketones investigated, the *o*-nitro isomers were preferentially attacked. The extent of reaction was found to depend on (1) the substrate, (2) the sulfur trioxide content of the oleum, (3) the final heating temperature, and (4) the reaction time.

To establish the mode of the degradation reaction, we attempted to identify the byproducts by extracting the aqueous acid phase of the nitration, as well as the caustic wash of the product, with methylene chloride and diethyl ether, but met with little success. Although as much as 40–50% of the dinitrobenzophenones were unaccounted for in some experiments, only small quantities of *m*- and *p*-nitrobenzoic acids were isolated (<5%). When a mixture of *o*- and *p*-nitrobenzoic acids was reacted with oleum (25 °C, 20% SO_3, 12 h), and then quenched with ice, most of the *p*-nitrobenzoic acid was recovered intact. None of the ortho isomer, however, was found. This suggests that most of the losses occurring during the treatment of ketones with

(11) Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051.

oleum are probably due to the formation of water-soluble sulfonation products, which are too reactive to be isolated.

Treatment of isomeric dinitrobenzophenone isomers with Sulfan (B) in ethylene dichloro led to the preferential reaction of *o*-nitro isomers. This indicates that concentration of sulfur trioxide, rather than acidity, is the controlling factor in the degradation reaction. The preferential nature of the reaction is attributed to the *o*-nitro group activation of the benzene ring toward the electrophilic substitution, owing to the nucleophilic character of the oxygen atom of the nitro group under protonating reaction conditions.[12]



R = *m*-O_2NPh, *m*-O_2NPhCO, CH_3

Experimental Section

Nitration in Fuming Nitric Acid. A total of 1200 g of 90% nitric acid was heated to 70 °C in a 2-L resin pot, and 200 g of benzophenone was added with stirring in increments over 1 h, while the temperature was maintained at 70 °C. After the addition was completed, the temperature was raised to 90 °C for 3 h. The reaction mixture was cooled, poured over 2 kg of cracked ice–water mixture, and filtered. The solids were washed with water (500 g) and digested in a Waring blender with 1 L of 10% sodium hydroxide solution. The solids were collected by filtration, washed four times with 500-g portions of water, and dried in a vacuum oven (100 °C, 16 h) to give 298 g (100%) of white product. The isomeric distribution of dinitrobenzophenones was determined by HPLC with a Varian Model 5000 liquid chromatograph. Analysis was carried out by using an alkylnitrile-bonded phase packing (10 μm particle size) in a 25 × 0.25 cm column. Isocratic elution with a *n*-hexane–methylene chloride–2-propanol mixture (15:82.5:2.5 by volume) at 1 mL/min gave separation of all six isomers at 30 °C, although the *o,p'* isomer was absent in our product. The order of elution followed the following sequence: *p,p'*-, *m,p'*-, *o,p'*-, *m,m'*-, *o,m'*-, and *o,o'*-dinitrobenzophenones. The analysis is reported in Table I.

Nitration in Fuming Sulfuric Acid. Preparation of Nitrating Mixture. A total of 165 g of 90% nitric acid was added dropwise with stirring and cooling to 573 g of oleum (22.5% SO_3), maintaining a temperature during addition below 20 °C.

Nitration. Benzophenone (200 g) was dissolved in 1910 g of oleum (22.5% SO_3), maintaining a temperature during addition around 20 °C. To this stirred mixture was added dropwise the nitrating mixture over 2 h at 15–20 °C. The reaction was then stirred for 0.5 h at room temperature and then heated to 70 °C for 1 h. After cooling, the reaction mixture was worked up as before. A total of 252 g (84%) of tan product was obtained containing 93.7% of the *m,m'*-dinitrobenzophenone. The final concentration of sulfur trioxide was estimated at 12%.

The above procedure was repeated with using 200 g of benzophenone, 165 g of 90% nitric acid, and 2500 g of oleum (33% SO_3). After the reaction mixture was heated to 70 °C for 0.2 h, 179 g (60%) of product was recovered containing 93.5% of the *m,m'*-dinitrobenzophenone.

In the final experiment, 200 g of benzophenone, 1260 g of oleum (33% SO_3), and 165 g of 90% nitric acid were reacted as above. With the reduced amount of oleum, however, it required 2 h at 80 °C for the *o,m'*-dinitro isomer to degrade. On workup, 232 g (77%) of product was isolated, containing 93.5% of desired isomer.

Nitration of 1,1-Diphenylethane. Into a 3-L, three-necked, round-bottomed flask, equipped with a mechanical stirrer, thermowell, and an addition funnel, was added 2550 g of 85% nitric acid (1610 mL of 90% HNO_3 and 140 mL of water), which was then cooled to 5–10 °C. To the stirred acid solution was added 280 g of 1,1-diphenylethane over 2.5 h, maintaining the temperature during addition below 10 °C. After the addition was completed, the product was allowed to warm to room temperature and was stirred for 30 min. It was then poured over ice–water and extracted with toluene. The organic layer was then washed with water, with 5% sodium hydroxide solution, and again with water. After being dried (anhydrous $MgSO_4$), the product was taken to dryness in a rotary evaporator to give a partially crystallized dark red oil, 389 g (93%).

Oxidation of Nitrated 1,1-Diphenylethane. A total of 135 g of nitrated diphenylethane was charged into a 1-L, 316 stainless-steel autoclave, followed by 200 g of water. The autoclave was heated to 170 °C and maintained at that temperature while 170 mL of 70% nitric acid was added over 1.5 h. When the addition of acid was complete, the reaction was allowed to proceed at 170 °C for 30 min, developing a final pressure of 450 psig. After the reaction mixture was cooled a total of 111 g of yellow solids was obtained by filtration (82%). Analysis by HPLC showed the following composition of dinitrobenzophenone isomers: *p,p'*, 57.9%; *m,p'*, 13.3%; *o,p'*, 25.0%; *o,m'*, 3.0%; *o,o'*, 0.8%.

Reaction of Nitro Aromatic Ketones with Oleum. A total of 50 g of the dinitrobenzophenones prepared above was added to 200 mL of oleum (15% SO_3), and the solution was heated with stirring to 70 °C. A sample was taken, and heating was continued for 1 h. The product was poured over ice–water, filtered, and washed two times with 10% sodium hydroxide solution (200 mL) and two times with water. After the product was dried in a vacuum oven (90 °C, 16 h), a total of 31.1 g (62%) of tan product was recovered. Analysis by HPLC showed only two dinitrobenzophenone isomers: *m,p'*, 18.3%; *p,p'*, 81.7%.

Registry No. *o,o'*-Dinitrobenzophenone, 51727-42-5; *o,m'*-dinitrobenzophenone, 60191-42-6; *m,m'*-dinitrobenzophenone, 21222-05-9; *m,p'*-dinitrobenzophenone, 1469-74-5; *p,p'*-dinitrobenzophenone, 1033-26-7; *o,p'*-dinitrobenzophenone, 79172-41-1; benzophenone, 119-61-9; 1,1-diphenylethane, 612-00-0.

(12) Szmant, H. H.; Harmuth, C. M. *J. Am. Chem. Soc.* **1959**, *81*, 962.

Electrochemical Reduction of Epoxy Ketones

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Received May 19, 1981

Hitherto, particularly in steroids, reductions of epoxy-keto systems for generation of a hydroxy ketone have been effected with reducing agents such as chromous ions,[1] or aluminum amalgam,[2] or palladium on barium sulfate with cyclohexene.[3] Our experiences with chemical reductive processes, particularly those with chromous salts and palladium, prompted us to investigate an alternative process.

To our knowledge electrochemistry has not previously been utilized for the transformation of epoxy ketones to hydroxy-keto systems. We report the successful application of the concept of electrochemical reduction for these systems. As will be noted, yields are relatively low, but we consider this point to be of secondary consideration for the purpose of this report.

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(2) (a) A. M. M. Hossain, D. N. Kirk, and G. Mitra, *Steroids*, **27**, 603 (1976); (b) D. N. Kirk and M. L. Sae Melo, *ibid.*, **34**, 683 (1979).
(3) (a) Von R. Imhof, E. Gossinger, W. Graf, W. Schnuriger, and H. Wehrli, *Helv. Chim. Acta*, **54**, 2775 (1971); (b) E. Gossinger, W. Graf, R. Imhof, and H. Wehrli, *ibid.*, **54**, 2785 (1971).

0022-3263/81/1946-5017$01.25/0