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Isomer Distribution in the Aluminum Chloride–Catalyzed Benzoylation of Toluene in Nitrobenzene[1–3]

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Pure samples of *o*-, *m*-, and *p*-methylbenzophenone were synthesized and a procedure developed for the infrared analysis of mixtures of these three components. The method was applied to the product obtained in the aluminum chloride-catalyzed reaction of benzoyl chloride with toluene at 25° in nitrobenzene solution. The results indicate the following isomer distribution: *ortho*-, 7.2%; *meta*-, 1.1%; *para*-, 91.7%. The presence of the *ortho*- isomer was confirmed by the preparation and isolation of solid derivatives. It was demonstrated that the reaction products do not undergo isomerization under the conditions of the benzoylation reaction. Consequently, the observed isomer distribution can be taken as a measure of the relative rates of reaction at the *ortho*-, *meta*-, and *para*- positions. The low yield of the *ortho*- isomer suggests that the substituting species must have large steric requirements. The large *para*-/*meta*- ratio indicates that the benzoylation reaction must be one of high selectivity.

The Friedel-Crafts acylation of simple monosubstituted benzene derivatives is commonly considered to result only in *para*-substitution.[5] Early reports exist of the formation of small amounts of the *ortho*- isomer during the benzoylation of toluene.[6,7] However, more recently it has been claimed that the acetylation and benzoylation of toluene result in the exclusive formation of the *para*- isomer.[8,9] No reports exist of the formation of the *meta*- isomer in the acylation of toluene,[10] although it has been reported recently that the acetylation of *t*-butylbenzene at 0° results in the formation of 1.8% of the *meta*- and 98.2% of the *para*- acetyl derivatives.[11]

Recently a quantitative relationship was proposed between the "activity" of a substituting agent, as measured by log ($k_{toluene}/k_{benzene}$) or log p_f, and its "selectivity," as measured by log (*para*-/*meta*-) or log (p_f/m_f).[12,13] In the acetylation reaction, toluene has been reported to react 8.35 and 13.3 times as fast as benzene.[14,15] On the basis of the proposed relationship, a yield of approximately 5% of the *meta*- isomer would be expected for a toluene/benzene ratio of this magnitude.

In view of the failure of numerous workers to observe any *meta*- isomer, a careful examination of this reaction appeared desirable. Accordingly, we undertook to establish the isomer distribution and the toluene/benzene rate ratio with high precision

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(3) Based upon a thesis submitted by Herbert L. Young in 1956 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Standard Oil Co. (Indiana) Fellow at Purdue University, 1953–1955.

(5) C. A. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry*, Reinhold Publishing Corp., New York, N. Y., 1941, p. 206.

(6) E. Elbs, *J. prakt. Chem.* [2], **35**, 466 (1887).

(7) W. D. Cohen, *Rec. trav. chim.*, **38**, 113 (1919).

(8) R. Pajeau, *Bull. soc. chim.* [5], **13**, 544 (1946).

(9) E. Koike and K. Okawa, *J. Chem. Soc. Japan*, **75**, 85 (1954).

(10) A number of examples of *meta* orientation have been described in the acylation of *alpha* substituted toluenes in which the *alpha* substituents are *meta* directing. W. Borsche and F. Simm, *Ann.*, **553**, 260 (1942); F. Kunckell, *Ber.*, **39**, 3145 (1906); D. Papa, E. Schwenk, and A. Klingsberg, *J. Am. Chem. Soc.*, **68**, 2133 (1946).

(11) J. C. Butler, L. L. Ferstandig, and R. D. Clark, *J. Am. Chem. Soc.*, **76**, 1906 (1954).

(12) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

(13) H. C. Brown and C. W. McGary, *J. Am. Chem. Soc.*, **77**, 2300 (1955).

(14) Y. Ogata and R. Oda, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **21**, 728 (1942).

(15) H. F. McDuffie and G. Dougherty, *J. Am. Chem. Soc.*, **64**, 297 (1942).

in order to test whether the acylation reaction constitutes a possible exception to the proposed quantitative treatment. In view of the higher volatility and lower stability of acetyl chloride as compared to benzoyl chloride, we selected the latter acylating agent for study.

RESULTS

Infrared spectroscopy was used for the analysis of the isomeric methylbenzophenones in the reaction product. This procedure required the synthesis of the three isomeric ketones in high purity for use as infrared standards. The physical properties of these derivatives are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS OF *o*-, *m*- AND *p*-METHYLBENZOPHENONES

	Methylbenzophenones		
	ortho	*meta*	*para*
Freezing point, obsd., °C.[a]	11.81	glass	56.94
Freezing point, calcd., °C.[a,b]	11.84		57.00
Purity, mole %[a]	99.9		99.9
M.p., °C.		0–2	
B.p., °C. (mm.)	162.2 (10)	172.4 (10)	177.4 (10)
	185.5 (25)	195.8 (25)	199.9 (25)
	205.0 (50)	214.9 (50)	218.6 (50)
n_D^{20}	1.5949[c]	1.5993[d]	
d_4^{25} g./ml.	1.0829	1.0832[e]	
M.p. of 2,4-dinitrophenylhydrazone	198.5–199.5[f]	221–222[g]	236–237[h]
M.p. of oxime	108–109[i]		

[a] Cooling curve data; mean value of two determinations. [b] Freezing point corrected to 0% impurity. [c] E. Koike and K. Okawa, *J. Chem. Soc. Japan*, **75**, 85 (1954) report n_D^{20} 1.5895. [d] E. Koike and K. Okawa, *loc. cit.*, report n_D^{20} 1.5982; J. W. Melton and H. R. Henze, *J. Am. Chem. Soc.*, **69**, 2018 (1947) report n_D^{20} 1.5970. [e] J. W. Melton and H. R. Henze, *loc. cit.*, report d_4^{20} 1.095. [f] M. S. Newman and C. D. McCleary, *J. Am. Chem. Soc.*, **63**, 1537 (1941) report m.p. 184–190°. [g] M. S. Newman and C. D. McCleary, *loc. cit.*, report m.p. 220.4–221.4°. [h] W. S. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934) report m.p. 199–200°. [i] I. I. Lapkin and A. V. Lyubimova, *J. Gen. Chem.* (*U.S.S.R.*), **19**, 707 (1949) report m.p. 104–105°.

The infrared spectra of the individual methylbenzophenones indicated differences sufficiently characteristic to be promising for the analysis of isomeric mixtures. Synthetic mixtures were prepared and analyzed successfully.

Nitrobenzene has frequently been utilized to provide homogeneous conditions for acylation reactions. Accordingly, the benzoylation of toluene was carried out at 25° in this solvent employing benzoyl chloride and aluminum chloride. The higher boiling methylbenzophenones were separated from the nitrobenzene solvent by fractional distillation. Yields of 87–96% of the isomeric methylbenzophenones were obtained in reaction times of 2.5–5.5 hr.

There is some evidence for the isomerization of aromatic ketones in the presence of hydrogen chloride and excess aluminum chloride.[16] It was therefore necessary to test the possibility of isomerization under the conditions adopted for the acylation reaction. Accordingly, pure samples of the methylbenzophenones were dissolved in nitrobenzene together with aluminum chloride, benzoyl chloride, and hydrogen chloride to give a solution related in composition to the acylation reaction mixtures. After reaction periods of 6.5–25 hours at 25°, the products were isolated and analyzed by infrared spectrophotometry. As far as could be ascertained, the spectra were identical with those of the materials introduced. It was concluded that isomerization is not a factor under the reaction conditions.

Infrared analyses pointed to the presence of approximately 92% of the *p*- and 8% of the *o*-, with but traces of *m*-methylbenzophenone indicated. Upon balancing out the absorption of the *ortho*- and *para*- isomers by means of a suitable standard mixture in the reference cell of the double-beam spectrophotometer, small but definite absorption bands appeared at 8.3, 10.5, 12.9 and 14.0μ. Since these are characteristic absorption bands for the *meta*- isomer, its presence in the reaction mixture was thereby established. However, the compound was evidently present in quite small amounts. After considerable experimentation, it became apparent that a precise analysis of the minor components, especially the *meta*- isomer, would require the separation of a considerable portion of the predominant *para*- isomer.

Fractional distillation was examined. A typical benzoylation reaction product was carefully distilled under reduced pressure in a column rated at 100 theoretical plates. There was obtained a small fraction (~5%) which distilled at a lower temperature than that of the *para*- isomer. The identity of this fraction as *o*-methylbenzophenone was confirmed by the preparation of its oxime and 2,4-dinitrophenylhydrazone (Table I) and mixed melting points of the derivatives with authentic samples. Unfortunately, the distillation proved difficult and we were unable to achieve clear-cut separation into definite plateaus. Consequently, this approach was abandoned.

p-Methylbenzophenone melts at 57°, considerably higher than the other isomers. It proved possible to utilize a series of repeated fractional crystallizations to achieve the separation of 75–85% of the material as the pure *para*- isomer. The mother liquor, now greatly enriched in the *ortho*- and *meta*- isomers, could now be successfully analyzed for the three isomers by infrared. The results of five individual preparations and analyses are presented in Table II.

The isomer distributions were determined for reaction mixtures containing aluminum chloride

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[16] G. Baddeley, *Quarterly Reviews*, **8**, 355 (1954) and references there cited.

TABLE II

ISOMER DISTRIBUTION IN THE ALUMINUM CHLORIDE-CATALYZED REACTION OF BENZOYL CHLORIDE WITH TOLUENE AT 25° IN NITROBENZENE SOLUTION

Initial Concentration of Reactants, *M*			Methylbenzophenone Product			
Benzoyl chloride	Aluminum chloride	Toluene	*Ortho-*	*Meta-*	*Para-*	Yield, %
0.66	1.3	1.3	8.0	1.0	91.0	96.0
1.0	1.0	1.0	7.4	1.2	91.4	87.0[a]
0.57	1.1	1.1	6.8	1.1	92.1	89.5
0.95	0.95	1.4	7.4	1.2	91.4	88.0
0.24	0.47	0.47	6.6	1.1	92.3	90.0
		Mean	7.2 ± 0.4	1.1 ± 0.1	91.7 ± 0.5	

[a] Additional 4.9% of benzoyl chloride accounted for (recovered as benzoic acid).

($AlCl_3$) and benzoyl chloride in a molar ratio of 1.0 and 2.0. Since the isomer distribution appeared to be independent of this ratio, all of the values obtained were utilized to calculate a mean product composition (Table II).

DISCUSSION

The identification of 7.2% of *o*- and 1.1% of *m*-methylbenzophenone in the product demonstrates that the acylation reaction is predominantly, but not exclusively, *para* substituting.

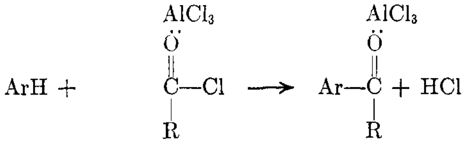
The small amount of *ortho* isomer suggests that the substituting species must be one of large steric requirements. It has been suggested frequently that the function of the aluminum chloride in the acylation reaction is to ionize the acyl halide, followed by an attack of the acylonium ion on the aromatic.[17,18]

$$RCOCl + AlCl_3 \longrightarrow RCO^+ + AlCl_4^-$$

$$RCO^+ + ArH \longrightarrow RCOAr + H^+$$

The large steric requirements exhibited by the reaction suggests that the attacking species cannot be the simple acylonium ion. The steric requirements of such an ion would be expected to be no greater than those of the isopropyl cation. Yet isopropylation of toluene results in the formation of 26.2% of the *ortho-* isomer.[19]

The addition compounds of aluminum chloride with acid chlorides are now believed to have the metal halide coordinated with oxygen atom of the carbonyl group.[20] A direct attack of this addition compound on the aromatic would be far more consistent with the observed large steric factor.[21]



$$ArH + \underset{\underset{R}{|}}{\overset{\overset{\overset{AlCl_3}{\ddot{O}}}{\|}}{C}}\text{—}Cl \longrightarrow Ar\text{—}\underset{\underset{R}{|}}{\overset{\overset{\overset{AlCl_3}{\ddot{O}}}{\|}}{C}} + HCl$$

The high *para-/meta-* ratio indicates that the benzoylation reaction must be a highly selective one. The yield of 98.2% of *para-* and 1.8% of *meta-* in the acetylation of *t*-butylbenzene[11] suggests that acetylation must also be highly selective, although somewhat less so than benzoylation.[22] These conclusions are not in accord with the relatively low toluene/benzene rate ratios previously noted.[14,15] However, distributions and rate ratios are for different conditions and, for that reason, are not strictly comparable.

A procedure was recently proposed for calculating the partial rate factors (o_f, m_f, p_f) and relative rate of reaction (k_Tk_B) for any electrophilic substitution reaction of toluene solely from the isomer distribution.[19] The following relationships are used:

$$\log m_f = 0.309S_f$$

$$\log o_f^{23} = 1.310S_f + \log\left(\frac{\%\ ortho\text{-}}{2 \times \%\ para\text{-}}\right)$$

$$\log(k_T/k_B) = 1.310S_f - \log\left(\frac{6 \times \%\ para\text{-}}{100}\right)$$

The selectivity factor, S_f, is defined as $\log p_f/m_f$, but may be calculated directly from the isomer distribution,

$$S_f = \log\left(\frac{2 \times \%\ para\text{-}}{\%\ meta\text{-}}\right)$$

Using these relationships, the partial rate factors and the relative rate of benzoylation of toluene to benzene may be calculated from the observed isomer distribution (Table II):

$$o_f = 32.0$$
$$m_f = 4.9$$
$$p_f = 817$$
$$k_T/k_B = 149$$

The predicted relative rates of benzoylation differ markedly from the observed acetylation rates.[14,15] Recently, the rates of benzoylation of benzene and toluene in bromobenzene as solvent were measured.[24] The rate ratio at 40°, $k_T/k_B = 53$, is in better agreement, but still differs considerably from the predicted value of 149. A rate study under conditions identical with those utilized for the isomer

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[17] H. Meerwein, *Ann.*, **455**, 227 (1927).

[18] E. R. Alexander, *Ionic Organic Reactions*, John Wiley and Sons, New York, N. Y., 1950, p. 260.

[19] H. C. Brown and C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 6255 (1956).

[20] N. N. Lebedev, *J. Gen. Chem. U.S.S.R.*, **21**, 1788 (1951). B. P. Surz and I. Cooke, *Helv. Chim. Acta*, **37**, 1273 (1954). I. Cooke, B. P. Surz, and C. Herschmann, *Helv. Chim. Acta*, **37**, 1280 (1954).

[21] A detailed examination of the mechanism of the acylation reaction has been completed by Dr. Frederick R. Jensen and will be prepared for publication shortly.

[22] The *para-/meta-* ratios in the nitration of toluene (8.45) and *t*-butylbenzene (6.32) are quite similar. K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).

[23] When steric effects are not important, the alternative relationship, $\log o_f = 1.215S_f$, can be used.

[24] F. Smeets and J. Verhulst, *Bull. soc. chim. Belg.*, **63**, 439 (1954).

TABLE III

DATA FOR ISOMER DISTRIBUTION RUNS

Benzoyl Chloride		Aluminum Chloride		Toluene		Nitrobenzene, Ml.	Time, Hr.
Wt. (g)	Moles	Wt. (g).	Moles	Wt. (g.)	Moles		
77.9	0.554	146.7	1.10	101.6	1.10	600	2.5
422.3	3.00	400.3	3.00	276.3	3.00	2170	3.5
111.3	0.792	201.1	1.58	145.9	1.58	1030	3.0
146.0	1.04	138.7	1.04	144.9	1.57	760	5.5
62.8	0.446	118.8	0.892	82.2	0.892	1670	4.7

distribution appeared desirable to test the accuracy of the predictions. Such a study is reported in the following paper.

EXPERIMENTAL

Materials. The bromotoluenes were the purest available commercial products. They were fractionated in a column rated at 50 theoretical plates. Center fractions which exhibited constant b.p. and n_{D}^{20} were utilized. The purities were established by cooling curves. The following constants and purities were observed: *ortho-* n_{D}^{20} 1.5562, 99.6 mole %; *meta-*, n_{D}^{20} 1.5528, 99.3 mole %; *para-*, m.p. 26.6°, 99.9 mole %.

Benzoyl chloride was fractionated at reduced pressure in an all-glass system: b.p. 74–76° (7.5 mm.), n_{D}^{20} 1.5333. Toluene was distilled over calcium hydride, b.p. 110°, n_{D}^{20} 1.4964. Nitrobenzene was distilled twice at atmospheric pressure, the center 75% cut being retained, b.p. 209–210°, n_{D}^{20} 1.5525, purity 99.8–99.9 mole % by cooling curve. Carbon disulfide, used for the infrared spectra, was purified by distillation over mercuric chloride.

Aluminum chloride (Baker's Analyzed Grade, Anhydrous) was sublimed several times in an all glass apparatus at reduced pressure (30–50 mm.). The sublimate was obtained as a pure white crystalline product, and was stored as loose plugs in sealed ampules.

The tolyl cadmium derivatives were prepared from the corresponding Grignard reagents and anhydrous cadmium chloride and were treated with benzoyl chloride following the procedure of Cason and Prout.[25] The reactions were carried out on a 1.0 mole scale. After hydrolysis, the crude products were recovered by distillation under reduced pressure in yields of 60–70%. The ketones were carefully purified by fractional distillation (and fractional crystallization for the *para-* isomer) until all fractions exhibited constant b.p., constant n_{D}^{20} (±0.0001), and identical infrared spectra. The physical properties are summarized in Table I.

Cooling curves. The melts were quite viscous and crystallization relatively slow. By utilizing a small temperature differential, 25–30°, a satisfactory curve was readily obtained for the *para-* isomer. However, both the *ortho-* and *meta-* isomers tended to solidify to glasses and to crystallize only with great difficulty. The existence of true crystalline phases with sharp melting points could be observed on small samples. Satisfactory cooling curves were finally realized for the *ortho-* isomer by employing a very slow cooling rate, extending the cooling curve over a period of 8 hr. Even this expedient did not help in the case of the *meta-* derivative. However, the three isomers were prepared by identical procedures, and in view of the high purities realized for the other isomers, we believe that the *meta-* derivative must be of comparable purity.

Derivatives. The 2,4-dinitrophenylhydrazones were prepared by a standard procedure.[26] In view of the discrepancies with literature values for the melting points, elementary analyses were made. These agreed closely with the calculated values. It is possible that we isolated different geometrical isomers than those obtained by the earlier workers (Table I).

The oxime of the *ortho-* isomer was readily prepared[26] and melted sharply. The *meta-* and *para-* derivatives did not give satisfactory melting points—they presumably consist of a mixture of the two geometric isomers.

Procedure for the benzoylation of toluene. Consideraleb experimentation was required to develop a procedure which yielded consistent results. Accordingly, the general procedure which was developed and used will be described in detail.

A 2-l., three-necked flask, equipped with a sealed (Tru-bore) stirrer and a nitrogen inlet, was thoroughly dried by heating with a flame in a stream of dry nitrogen. Sealed ampoules of aluminum chloride, encircled at one end with a file scratch, were touched with a hot rod in such a way as to crack, but not break, the ampoule. The end of the ampoule was placed in the open neck of the flask, the top broken off, and the loose plug of aluminum chloride transferred into the flask. Nitrobenzene (over calcium hydride) was siphoned through a glass filter stick into the flask. When the aluminum chloride had largely dissolved, benzoyl chloride was added. The flask was then immersed in a water bath (25 ± 1°) and the orange-yellow solution brought to reaction temperature. The reaction flask was equipped with an addition funnel having an equilizer side arm and the reaction was initiated by the rapid addition (8–15 min.) with stirring of toluene. The reaction mixture changed in color from the original orange-yellow to an orange-red. After 10 min., the funnel was replaced by a thermometer well and thermometer. In all cases the temperature remained at 25°. All operations were carried out with a constant dry nitrogen atmosphere.

The data of the various runs are summarized in Table III.

After an appropriate reaction period, the reaction mixture was poured into excess 4*N* sodium hydroxide and the mixture was heated under reflux for 2.5 hr. Two clear phases resulted. (Without this precaution, some derivative of benzoyl chloride, probably benzoic anhydride, contaminated the methylbenzophenone product and interfered with the subsequent infrared analysis.) The nitrobenzene layer was separated and washed with 500 ml. of water, which was added to the basic aqueous phase. The aqueous phase was then extracted with three 500-ml. portions of ether. The original nitrobenzene phase, to which was added 500 ml. of ether, and the combined ether extracts were washed (in that order) with 250 ml. portions of 3*N* hydrochloric acid, water, and saturated sodium chloride solution, and finally dried over anhydrous magnesium sulfate. The bulk of the ether was removed by distillation and the residue fractionated through a 50-cm. heated column. The nitrobenzene and ketone fractions were taken off at reduced pressure. Infrared examination of the last nitrobenzene fractions insured that none of the product was being lost in these fractions. A small intermediate fraction containing both nitrobenzene and ketone was saved for infrared analysis. Small aliquots of the product were removed and stored.

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(25) J. Cason and F. Prout, *Org. Syntheses*, **28**, 75 (1948).

(26) R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, Inc., New York, 1948.

The products were melted and placed in a constant temperature bath at 45 ± 0.3°, seeded with the *para-* isomer, and allowed to crystallize slowly (10–35 hr.). The mother liquor was then decanted and the crystalline material remelted and recrystallized at 48°. The operation was repeated at 51°, 54°, and 55.5°. The final crystalline material was stored and the combined mother liquors were melted and subjected to another series of such crystallizations. With each succeeding series of crystallizations, the initial crystallization temperature was lowered and the quantity of the final crystalline phase sharply decreased. The sixth and final series of crystallizations was carried out at 35°, 40°, 45°, 50°, 54° and 55.5°.

The *para-* isomer was obtained as large, translucent prisms, m.p. 56–57°, indistinguishable by infrared spectrophotometry from the 99.9% material. The mother liquors were distilled at reduced pressure through a small 10-cm. column, and the minute residue recovered for infrared analysis. Losses in this series of operation were quite low, usually less than 2%.

Infrared analyses. The infrared spectra (7–15μ region) were obtained with a double beam Perkin-Elmer recording spectrophotometer, Model 21. All samples were dissolved in carbon disulfide. Matched cells (thickness: 0.10 mm.) were used with carbon disulfide in the reference cell. When the "differential" method was used for the analysis of the *meta-* isomer, a suitable standard mixture, dissolved in carbon disulfide, was placed in the reference cell. The intensities were measured in terms of % transmission: the "base line" technique was used to determine the value of T_0. The spectra of a set of standard mixtures were determined along with each group of unknown samples. Calibration curves were then constructed and used to determine the concentrations of the components in the unknown mixtures.[27]

The compositions of the intermediate fractions were determined by use of two standard mixtures of *o-* and *p-*methylbenzophenone containing 10–20% nitrobenzene. The residues were shown to be the *para-* isomer by their infrared spectra. The concentrations of the *ortho-* and *para-* isomers in the mother liquors were determined by the use of three standard mixtures, total concentration 0.5 gm./5 ml., containing about 3.5% (0.017–0.019 gm./5 ml.) of the *meta-* isomer. The following absorption bands were used: *ortho-*, 13.2μ and *para-*, 12.0μ. Both bands are of strong intensity and are essentially free of interference from the other isomers.

The concentration of the *meta-* isomer in the mother liquors was determined by the "differential" procedure, in which the absorptions of the *ortho-* and *para-* isomers were balanced out by means of a suitable standard mixture in the reference cell.

A second procedure was also used. The spectra of the series of standard mixtures and unknown samples were redetermined with pure carbon disulfide in the reference cell. The absorption band at 8.3μ is of medium intensity and is characteristics of the *meta-* isomer. However, at the high concentrations used in the analysis the *para-* isomer also has an appreciable absorption at this wave length. The optical density of the 8.3μ band was therefore corrected for the *para-* contribution and then used for the analysis of the *meta-* isomer. The correction was simply the optical density at 8.3μ of the special reference sample, since the concentration of the *para-* isomer was the same in all the standard and unknown mixtures.

Both types of analyses were repeated with a second series of standard mixtures. In all, seven determinations of the *meta-* isomer were made for each of the last three runs.[28] The percentage of the *meta-* isomer was calculated from its estimated concentration and the actual total concentration of the sample. The precision realized is indicated by the data in Table IV.

TABLE IV

SUMMARY OF *Meta-* ISOMER DETERMINATIONS

Band (μ)	Procedure	% Meta Detn. 3	Detn. 4	Detn. 5
8.3	Differential	3.0	3.9	3.1
12.9	Differential	3.8	4.4	3.6
14.0	Differential	3.5	4.3	2.7
12.9	Differential	3.5	4.1	3.5
14.0	Differential	2.9	4.1	2.6
8.3	*Para-* isomer correction	2.9	4.3	2.8
8.3	*Para-* isomer correction	2.9	4.0	2.8
Mean values		3.2 ± 0.3	4.2± 0.2	3.0 ± 0.3

TABLE V

COMPOSITION OF METHYLBENZOPHENONE PRODUCTS

	Weight (g.)								
	Detn. 3			Detn. 4			Detn. 5		
Fractions	*Ortho-*	*Meta-*	*Para-*	*Ortho-*	*Meta-*	*Para-*	*Ortho-*	*Meta-*	*Para-*
Intermediate	1.16	...	4.6	3.06	...	8.2	1.09	...	3.6
Main	8.35	1.58	122.0	10.2	2.24	155.0	4.10	0.845	67.9
Residue	...	...	1.4	...	...	0.9	...	...	1.3
Total	9.51	1.58	128.0	13.3	2.24	164.1	5.19	0.845	72.8
Total ketone			139.1			179.6			78.8
Theoretical yield			155.4			204.0			87.5
% Yield			89.5			88.0			90.0

The mean values of the *meta-* percentage and the *ortho-* and *para-* percentages were totaled and normalized to a basis of 100%. These results provided the compositions of the mother liquors. The compositions of the main product fractions were then calculated from the compositions of the mother liquors and the enrichment factors from the fractional crystallizations. From these results and the weights of the isomers present in the intermediate fraction the complete compositions of the products could be calculated. The distribution in the last three runs is shown in Table V.

The results for the complete analyses are summarized in Table II.

LAFAYETTE, IND.

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[27] For a more complete description of the infrared analyses consult the Ph.D. thesis of H. L. Young, Purdue University Library.

[28] The procedure utilized in these three runs was developed as a result of our experience in the first two runs (Table II) and represents an improvement over that used in the earlier analyses. Since identical results were realized by both procedures, only the later, improved analytical procedure is here described.