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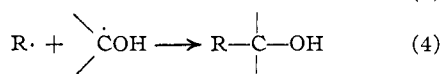
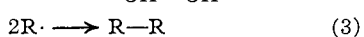
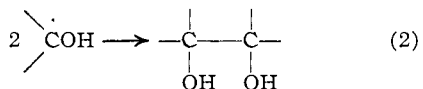
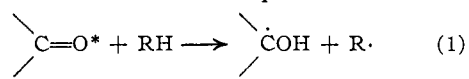
Mechanisms of Photoreactions in Solution. II. Reduction of Benzophenone by Toluene and Cumene

BY GEORGE S. HAMMOND, WILLIAM P. BAKER AND WILLIAM M. MOORE

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The photoreduction of benzophenone by toluene and cumene has been analyzed quantitatively. Paramagnetic metal chelate compounds have powerful quenching effects. The data are interpreted in terms of the reactivity of the triplet state of benzophenone, and rate constants for all processes are estimated. Preliminary measurements of the reactivity of other ketones have been made using toluene as the reductant.

The photoreduction of ketones by a variety of hydrogen donors has been reviewed by Schönberg and Mustafa.¹ Included among the donors are various hydrocarbons. In most instances, in which qualitative observations indicate that the reaction "goes well," the donor has a structure such that it should yield a relatively stable free radical upon loss of a hydrogen atom. A full material balance usually has not been carried out but qualitative observations suggest that an excited state of the carbonyl compound extracts hydrogen from the reductant and that the ultimate reaction products are formed by coupling reactions of the radicals produced in the first step.

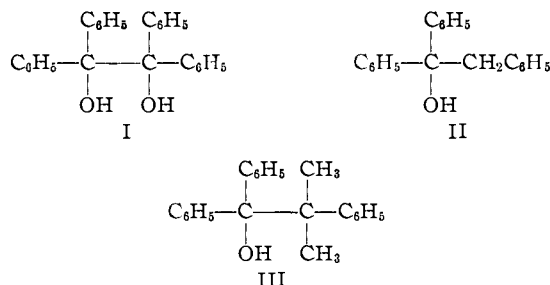


We have carried out quantitative studies of several reactions of this type. The quantum yields of the various possible processes have been measured and the quenching technique, developed in the accompanying paper,² was used to make a preliminary estimate of the lifetime of the triplet state of benzophenone in toluene and cumene.

Results and Discussion

Large batches of benzophenone in toluene and in cumene were photolyzed by prolonged exposure to sunlight. The mixtures were then worked up by conventional techniques. It was found that benzopinacol (I) and benzyldiphenylcarbinol (II) accounted quantitatively for the benzophenone photolyzed in the toluene mixture. Bibenzyl, which should have been formed in amount equivalent to benzopinacol, was detected as a reaction product but was not isolated quantitatively. Separation of the products formed in cumene gave benzopinacol, the tertiary carbinol (III), and 1,2-diphenyl-1,2-dimethylbutane (bicumyl).

Quantitative analyses of photolysis mixtures were carried out by spectrophotometric determination of residual benzophenone and/or by determination of benzopinacol either gravimetrically or



by lead tetraacetate oxidation. Lead tetraacetate determination could not be used in runs with cumene as it was found that the tertiary alcohol, III, was cleaved rapidly by the reagent. This interesting observation will be reported in more detail elsewhere.

Quantum yields were determined by reference to the uranyl oxalate actinometer.³ Studies by two workers, using different filter systems, gave slightly different values for the quantum yields in the benzophenone-toluene reaction. These are identified as belonging to series A and series B in Table I. In the work with ketones the concentration conditions were such that all of the light was absorbed in all experiments. This condition will have no influence on the results if the mechanism of equations 1-4 is correct; however, if some unexpected chain reaction occurs, the results might vary with the steady-state concentrations of the radicals in the solution. In order to check the possible consequences of gradients in the radical concentrations in the solution, wire screens were interposed between the light source and the reaction cell. Although precision of such runs was not as good as usual, the results indicate that the quantum yields are not influenced by this operation.

Quantum yields in the benzophenone-toluene system were measured both at 25° and at 52.5°. Since the results were essentially identical, it was surmised that reaction 1 has no more than a small activation energy. Therefore, the water-bath used originally was replaced with an air-bath designed only to hold the temperature close to room temperature.

Table I presents representative data for the reduction of benzophenone in toluene, in cumene and in benzene solutions of toluene and diphenylmethane. Table II shows data for the reaction of other ketones with toluene. The low-quantum yields obtained with filter system 1 are attributable to the fact that this filter passed light down to

(1) A. Schönberg and A. Mustafa, *Chem. Revs.*, **46**, 181 (1947).

(2) G. S. Hammond, W. M. Moore and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(3) P. A. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

TABLE I
 QUANTUM YIELDS IN PHOTOREDUCTION OF BENZOPHENONE BY HYDROCARBONS

Run no.	Series	Filter system	Reductant	Initial benzophenone $\times 10^3$, moles/l.	% Conversion of benzophenone	Φ_{Ketone}	% Yield of pinacol
156-1 ^a	A	1	Toluene	101	14	0.19	67
159-1 ^a	A	1	Toluene	101	18	.21	64
173-1 ^b	A	1	Toluene	100	20	.19	72
175-1 ^b	A	1	Toluene	100	22	.21	70
173-2 ^b	A	1	Toluene	100	31	.22	67
168-3	A	1	Toluene	300	16	.19	63
171-2	A	1	Toluene	300	22	.22	72
177-1 ^c	A	1	Toluene	100	25	.21	65
177-2 ^c	A	1	Toluene	100	25	.21	67
55-2	A	2	Toluene	100	47	.35	..
61-4	A	2	Toluene	100	67	.38	..
32-1	A	2	Toluene	100	76	.36	61
32-2	A	2	Toluene	100	50	.36	62
59-4	A	2	Toluene	100	49	.35	61
101	B	2	Toluene	100	33	.39	..
102	B	2	Toluene	100	70	.40	..
103	B	2	Toluene	100	42	.38	..
104	B	2	Toluene	100	24	.41 ^d	..
105	B	2	Toluene	100	27	.40 ^d	..
106 ^c	B	2	Toluene	100	22	.36	..
113	B	2	Cumene	100	18	.18	36
114	B	2	Cumene	100	28	.19	44
116 ^c	B	2	Cumene	100	89	.74	46
117 ^c	B	2	Cumene	100	48	.69	46
118 ^c	B	2	Cumene	100	19	.70 ^d	..
64M-1	B	2	Diphenylmethane	100	57	.62	..
64M-2	B	2	Diphenylmethane	100	56	.65	..

^a $T = 26^\circ$. ^b $T = 52.5^\circ$. ^c Degassed solution. ^d Calculated using benzophenone-isopropyl alcohol actinometer.

 TABLE II
 PHOTOREDUCTION, BY TOLUENE, OF KETONES OTHER THAN BENZOPHENONE^a

Ketone	Original ketone $\times 10^3$, mole l. ⁻¹	% Conversion	Φ_{Ketone}	% Yield of pinacol
<i>p,p'</i> -Dimethoxybenzophenone	30.0	77	0.21	63
<i>p,p'</i> -Dimethoxybenzophenone	30.0	49	.20	67
<i>p,p'</i> -Dimethoxybenzophenone	74.8	52	.20	62
<i>p</i> -Cyanobenzophenone	100	37	.30	63
<i>p</i> -Cyanobenzophenone	100	36	.31	60
<i>p</i> -Cyanobenzophenone	100	36	.31	58
Acetophenone	100	44	.16	72
Acetophenone	100	47	.16	67
Acetophenone	100	29	.15	73

^a All run in toluene solution; benzophenone derivatives studied using filter system 2 and acetophenone with filter system 3.

2350 Å. so that some of the effective output of the arc was absorbed by toluene, which absorbs all light below 2700 Å. Except in runs that were stopped at very low conversions, the same results were obtained with toluene with and without degassing. The same was not true of the work with cumene, in which it was found that quantum yields were much higher in degassed solutions. This probably indicates that all oxygen is removed very rapidly from toluene solutions by virtue of the scavenging reaction of benzyl radicals. It is then possible that the less reactive cumyl radicals do not

scour the solution as rapidly, allowing the quenching effect of oxygen² to be observed. Trouble was experienced in the study of the reduction of *p,p'*-dimethoxybenzophenone with toluene unless the solutions were degassed. This effect is probably due to the fact that this ketone is less soluble than others used in the study. With relatively low concentrations of the ketone, significant measurements of quantum yield demanded that the reactions be stopped when relatively small amounts of ketone had been destroyed. This magnified the effects of small amounts of oxygen.

The purely chemical part of the mechanisms of these reactions seems to be very straightforward. The quantum yields were higher with diphenylmethane and cumene than with toluene although the differences are not great. From the data in the accompanying paper³ we can add the fact that benzhydrol and isopropyl alcohol are more reactive than the hydrocarbons. This sequence of reactivities is similar to that observed in chain-transfer reactions of the hydrogen donors with the growing radicals involved in vinyl polymerization.⁴

The behavior of the radicals is remarkably consistent. The yields of pinacol measured in this study ranged only from *ca.* 45% (benzophenone-cumene) to about 70% (acetophenone-toluene). We should not dare to attempt interpretation of those small variations that are observed. However, it is obvious that cage effects play no very important role in the reactions. Since two unlike

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 152.

radicals are produced in reaction 1, diffusion-controlled coupling would result in unsymmetrical products (e.g., III) rather than pinacols. In fact, if cage effects were to be of any considerable consequence, one might expect the yield of cross-coupling products to decrease as the radicals were made more stable. A contrary trend is observed if the reactions of cumene and toluene with benzophenone are compared. Cumyl radicals should be more stable than benzyl radicals so one would expect the yield of tertiary carbinol to be higher in the reaction of toluene if cage-coupling were of dominant importance. In actual fact, the yield of tertiary carbinol is higher in the reaction with cumene.

Consideration of the quantum yields in the reactions of benzophenone and its derivatives (Table II) shows that polar effects on the rate of reaction I must either be small or highly compensated by similar effects on the rates of deactivation reactions that compete with the chemical process. Attachment of either an electron-releasing or an electron-attracting substituent to the benzophenone molecule reduces the quantum yield. This suggests that polar effects on reaction 1 are minor.

We can exploit information gleaned from study of the reduction of benzophenone by benzhydrol² to carry out a preliminary quantitative analysis of the reactions of benzophenone with cumene and toluene. Table III shows the results of quenching experiments carried out with a number of paramagnetic metal chelate compounds. Aluminum dipivaloylmethide (DPM) has no appreciable effect on the reaction, indicating that the quenching effects of the other chelates is to be associated with the fact that they contain unpaired electrons. We inferred from study of the benzhydrol system that ferric DPM probably quenches benzophenone triplets on every encounter. Comparison of the data in Table III indicates that rare-earth chelates are not quite as reactive as the ferric compound. This result might have been anticipated on the basis of the studies of Porter and Wright,⁵ who observed quenching of naphthalene triplets by metallic ions.

TABLE III
QUENCHING PHOTOREDUCTION BY METAL CHELATE COMPOUNDS

Reductant	Metal dipivaloylmethide	Concn. of M(DPM) ₃	Φ_{Ketone}
Toluene ^c	None	None	0.36 ^a
Toluene ^c	Iron(III)	4×10^{-5}	.27 ^a
Toluene ^c	Aluminum	4×10^{-5}	.35 ^a
Toluene	None	None	.41 ^b
Toluene	Iron(III)	7×10^{-5}	.33 ^b
Toluene	Samarium	1×10^{-5}	.36 ^b
Toluene	Erbium	9×10^{-5}	.35 ^b
Cumene ^c	None	None	.70 ^b
Cumene ^c	Iron(III)	5×10^{-5}	.611 ^b

^a Using uranyl oxalate actinometry. ^b Using isopropyl alcohol-benzophenone as an actinometer. ^c Degassed solutions.

If it is assumed that the rate of quenching of benzophenone triplets by ferric DPM is about 2×10^9 liter mole⁻¹ sec.⁻¹, we can estimate rate con-

(5) G. A. Porter and M. R. Wright, *J. chim. phys.*, **55**, 705 (1958).

stants for the other processes in the cumene and toluene systems. It is not convenient to vary the concentrations of the hydrocarbons since they are not nearly as reactive as benzhydrol, so we have varied the concentration of the chelate. The appropriate rate law is given in equation 5

$$\frac{1}{\Phi} = 1 + \frac{k_d}{k_r[\text{RH}]} + \frac{k_Q[\text{Q}]}{k_r[\text{RH}]} \quad (5)$$

Table IV shows the data used to estimate the value of k_Q/k_r . It appears that the value of k_Q/k_r is of the order of 10^5 . This leads, in turn, to a value of k_r of 2×10^4 . By using data for quantum yields in benzene-toluene mixtures (no quencher), we can evaluate the relative efficiencies of the two solvents in deactivation of the triplets.

TABLE IV
REDUCTION OF BENZOPHENONE BY TOLUENE IN THE PRESENCE OF Fe(DPM)₃

Concn. Fe(DPM) ₃	Φ_{Ketone}	$1/\Phi_{\text{Ketone}}$	k_Q/k_r
None	0.35	2.86	
4×10^{-5}	.27	3.7	2.0×10^5
7×10^{-5}	.23	4.3	1.9×10^5
1×10^{-3}	.07	14	1.0×10^5
2×10^{-3}	.08	12	4.4×10^4

In order to express the results quantitatively, it is necessary to assume some molecularity of the deactivation process with respect to solvent molecules. Equation 6 shows the rate law obtained by treating the quenching reactions as monomolecular with respect to solvent molecules.

$$\frac{1}{\Phi} = 1 + \frac{k_d'[\text{C}_6\text{H}_5\text{CH}_3]}{k_r[\text{C}_6\text{H}_5\text{CH}_3]} + \frac{k_d''[\text{C}_6\text{H}_6]}{k_r[\text{C}_6\text{H}_5\text{CH}_3]} \quad (6)$$

Table V shows the quantum yields for benzophenone disappearance in benzene-toluene mix-

TABLE V
PHOTOREDUCTION OF BENZOPHENONE IN BENZENE-TOLUENE MIXTURES^a

Molarity of toluene	Molarity of benzene	Φ_{Ketone}^b	$1/\Phi$
9.4	0	0.38	2.63
7.0	2.6	.37	2.70
3.5	5.6	.33	3.04
2.3	8.4	.24	4.16
1.11	9.7	.18	5.55
0.75	10.1	.12	8.33

^a Using filter system 2, uranyl oxalate actinometry. ^b Averages of three or more determinations.

tures. Note that the treatment gives k_d' and k_d'' as bimolecular rate constants, in contrast to the values of k_d given previously as unimolecular rate constants. Treatment of the data by the method of least squares gives $k_d''/k_r = 0.4$. Since the limiting quantum yield in pure toluene is 0.38, the value of k_d/k_r is 1.6. The precision of these determinations is not high but is sufficient to show (a) that the rate of quenching does not depend strongly on the structure of the solvent and (b) toluene is a slightly better quencher than benzene. The value of k_d'' also can be compared with the rate constant for deactivation in benzene inferred from the study of the reduction by benzhydrol in benzene.² The value obtained for k_d was

$2.6 \times 10^5 \text{ sec.}^{-1}$. Since the molarity of pure benzene is $11.3 M$ the constant corresponds to a value of 2.3×10^4 for k_d'' as compared with the value of 0.8×10^4 calculated from the results with benzene-toluene mixtures. Values of the estimated rate constants are summarized in Table VI.

TABLE VI

ESTIMATED RATE CONSTANTS FOR REACTIONS OF BENZOPHENONE TRIPLETS IN HYDROCARBON SOLVENTS

Reaction	k , l. mole ⁻¹ sec. ⁻¹
Hydrogen abstraction from benzohydrol ^a	5×10^6
Hydrogen abstraction from toluene	2×10^4
Hydrogen abstraction from cumene	7×10^4
Deactivation by benzene (k_d'')	2.3×10^{4a} (0.8×10^4) ^b
Deactivation by toluene (k_d')	3×10^4

^a From reference 2. ^b From equation 6.

If we again assume that the yield of benzophenone triplets is quantitative, we can calculate the ratio of k_d/k_r for cumene from the quantum yield in pure cumene (0.70). The value is 0.43. If we assume that k_d for cumene is the same as that for toluene we obtain the value of 7×10^4 for k_r .

Experimental

Materials.—Acetophenone (Matheson, Coleman and Bell) was redistilled; b.p. 200° at 737 mm. Benzene (Baker and Adamson, Reagent Grade, Thiophene Free) was used without further purification. Benzophenone (Matheson, Coleman and Bell, Reagent Grade) was used without further purification.

Cumene (Eastman Kodak, White Label) was washed five times with concentrated sulfuric acid, once with water, once with 10% aqueous sodium carbonate, once again with water and was dried over anhydrous magnesium carbonate. The product was fractionally distilled over sodium, and the fraction boiling at 150 – 152° was collected and stored over sodium. Analysis by vapor phase chromatography indicated the presence of 1.6% of a low boiling impurity. *p*-Cyanobenzophenone, a student preparation, was recrystallized from ethanol; m.p. 115.5 – 116.5° . *p,p'*-Dimethoxybenzophenone (Eastman Kodak, White Label) was recrystallized from absolute ethanol; m.p. 144.5° . Lead tetraacetate (Matheson, Coleman and Bell, Reagent Grade) was dissolved in hot glacial acetic acid, and the insoluble lead oxide was removed by filtration. On cooling, the solution deposited white needles of lead tetraacetate. The freshly crystallized product was immediately dissolved in glacial acetic acid to prepare stock solutions for titrimetry.

Metal Chelates.—The preparation of Fe(DPM)₃ was described previously.² Erbium dipivaloylmethide was prepared by dissolving the oxide (Lindsay Chemical Division) in dilute, aqueous hydrochloric acid, followed by the addition of an equal volume of ethanol and finally by addition of an excess of dipivaloylmethane. Some precipitate was formed and dimethylformamide was added until the solution became homogeneous. Dilute aqueous ammonia then was added until the solution was neutral to litmus paper. The pink precipitate of erbium chelate was separated by filtration and dissolved in ligroin. Concentration of the ligroin solution resulted in deposition of pink crystals; m.p. 145 – 150° . Attempts to further purify the chelate by sublimation or recrystallization either led to decomposition or did not improve the purity. Elementary analysis showed that the product contained nitrogen, presumably from dimethylformamide. The ultraviolet spectrum of the material had maxima at 3750 \AA . (apparent molar extinction coefficient of 92) and at 2840 \AA . (apparent molar extinction coefficient of 28,000). Samarium dipivaloylmethide was prepared by the same procedure. The product, m.p. 188 – 191° , also contained dimethylformamide and could not be sublimed without decomposition.

Apparatus.—The apparatus used in the later part of this work has been described elsewhere.² The earlier work (runs in series A) was carried out with a reactor consisting of an 800 watt, high pressure mercury arc (Westinghouse), a collimating lens, filters as described below, reaction cells, a second lens to focus the exit beam and an Eppley thermopile. The lenses were the windows of a constant temperature bath that contained the filters and reaction cell. Various cells, of the general description given earlier,² were used in the work. Conventional, high velocity vacuum systems were used in degassing procedures.

Filter Systems.—When a water-bath was not used a water cell was placed before the principal filter cell. Filter 1 consisted of a solution made by mixing solutions prepared by dissolving 450 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 900 ml. of distilled water and 250 g. of $\text{CaSO}_4 \cdot 7\text{H}_2\text{O}$ in 830 ml. of distilled water. This filter passed a considerable amount of the incident light below 3000 \AA . Low values of the quantum yields with this filter system are due, at least in part, to absorption by the aromatic solvent. We hope to report later on the variation of the "true" quantum yield in photo-reduction reactions with the wave length of the exciting light.

Filter system 2, with slight modification, was used in both series A and series B measurements. It consisted of a solution made by dissolving either 250 g. or 400 g. of copper sulfate in one liter of distilled water and Corning filter No. 7-51. When the more concentrated copper sulfate solution is used this system has maximum transmittance at 3660 \AA . with a half-height band pass of 500 \AA . The system excludes completely the 3130 \AA . mercury line.

Filter system 3 was prepared by dissolving 450 g. of nickel sulfate hexahydrate in 900 ml. of 0.75% copper sulfate in distilled water. This filter has maximum transmission at 3100 – 3200 \AA . It also transmits a considerable amount of visible light, which may introduce errors in the conversion of thermopile readings to intensities if the oxalate actinometer is used as reference.

Reaction of Benzophenone with Toluene.—Fifteen-gram batches of benzophenone were dissolved in 120 ml. of toluene, sealed under vacuum in 26 ml. i.d. tubes and exposed to the late summer sunshine in Ames for periods of about four weeks. The products of the reaction were analyzed by the following scheme. Toluene was removed by addition of water and distillation of the azeotrope (b.p. 84° at 740 mm.). Skellysolve B (petroleum ether, b.p. 60 – 70°) was added to the residue and allowed to incubate for a period of 24 hr. or more. The residue was benzpinacol in essentially pure form. Unreacted benzophenone was separated from an aliquot portion of the mother liquor by oximation.⁶ Another aliquot from the Skellysolve B solution was separated by chromatography on alumina. The first eluate, with Skellysolve B, contained a small amount of bibenzyl. Elution with methanol gave benzyl-diphenylcarbinol. Residual benzophenone also was determined spectrophotometrically. Three batches were worked up completely. Yields of isolated products based on benzophenone consumed were: benzpinacol, 51, 51 and 50%; benzyl-diphenylcarbinol, 44, 38 and 46%. When bibenzyl was added to a reaction mixture no change was observed in the yields of the pinacol and tertiary alcohol; however, very little bibenzyl was recovered, indicating that this product is removed during the removal of toluene by distillation.

Reaction of Benzophenone with Cumene.—Solutions of benzophenone (0.5 M, 1.0 M and saturated) were degassed and sealed in Pyrex tubes. The tubes were exposed to summer sunshine in Pasadena for six weeks. White crystals began to deposit after the first week. The tubes were opened, the contents were transferred to a distilling flask and the cumene was removed by distillation under reduced pressure. The residues were mixed with ligroin (60 – 70°) and allowed to stand overnight. The precipitated benzpinacol (dec. p. 186°) was separated by filtration, weighed and dried. The ligroin was removed from the filtrate leaving an oil. Addition of methanol to the oil caused the precipitation of 1,2-dimethyl-1,2-diphenylbutane, m.p. 117 – 118° . The residual oil was weighed and was chromatographed to separate 1,1,2-triphenyl-2-methylpropanol, m.p. 62° . *Anal.* Calcd. for $\text{C}_{22}\text{H}_{20}\text{O}$: C, 87.6; H, 7.3. Found: C, 88.0; H, 7.9. The yield of the tertiary alcohol

(6) S. M. McElvain, "Characterization of Organic Compounds," 2nd Ed., The Macmillan Co., New York, N. Y., 1953, p. 204.

was determined by weighing the product after chromatography.

The yields of isolated products were essentially the same in all experiments: benzpinacol, 24%; tertiary alcohol, 48-60%; and hydrocarbon, 24%.

Procedures.—The general photochemical procedure was described earlier.² In the latter part of the work the photoreduction of benzophenone by isopropyl alcohol was used for actinometric measurements. It was found that the rates of reduction were reproducible and easily measured by spectrophotometric analysis for residual benzophenone. In fact, the best evidence to support the assignment of the quantum yield one to the photoreduction is found in the comparison of the quantum yields in the reduction of toluene based on uranyl oxalate actinometry with those based on the isopropyl alcohol reaction (Table I). The values determined by the isopropyl alcohol reduction are slightly higher than those measured by the oxalate method. Obviously we could assign a value of more than one to the alcohol reaction and bring the values into agreement; how-

ever, we do not have sufficient confidence in the precision of the oxalate procedure to justify such a correction.

Analyses.—Pinacols were determined by titration with lead tetraacetate² except in the work with cumene. The method was not applicable in that case because it was found that the tertiary alcohol produced in the reaction was also cleaved by the reagent. In the cumene work the yield of benzpinacol was determined gravimetrically after isolation by a procedure essentially the same as that described for the batch reactions. Residual ketone concentrations were determined spectrophotometrically. Readings of the absorbance of the analytical solutions (prepared by dilution of aliquots) were taken at several wave lengths and compared directly with samples of the original solutions which had not been irradiated.

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[CONTRIBUTION FROM THE POLYMER RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN]

Kinetics of Three-Compound Equilibrations. V. Concurrent Alkylation and Isomerization

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A study has been made of the monoalkyltoluene isomer distributions obtained by the Friedel-Crafts methylation, ethylation and isopropylation of toluene using a variety of catalysts and alkyl derivatives. All of the isopropyltoluene isomer distributions could have been obtained by alkylation to produce a mixture containing 42% *o*-, 21.5% *m*- and 36.5% *p*-isopropyltoluene and isomerization of this mixture. With the possible exception of ethylation with ethylene, all the ethyltoluene isomer distributions could have been obtained by alkylation to produce an initial mixture containing 48% *o*-, 18% *m*- and 34% *p*-ethyltoluene and isomerization of this mixture. Ethylation with ethylene appears to produce an initial isomer distribution somewhat lower in *p*-ethyltoluene than the above. Methylation of toluene with methyl chloride, methyl bromide or methyl alcohol produces a mixture containing 60% *o*-, 14% *m*- and 26% *p*-xylene. These results indicate that in the methylation, ethylation and isopropylation of toluene, the particular catalyst and derivative used influences only the extent of isomerization that accompanies the alkylation. For the above series of initial isomer distributions, the ratio of *p*-substitution to *m*-substitution is constant within experimental error so that methylation, ethylation and isopropylation have the same positional selectivity. Since equal selectivity implies equal reactivity, the enormous increase in absolute rates in the above series probably result from the quantity of activated alkyl derivative involved in each reaction and not the reactivity of the activated alkyl derivative involved in each reaction.

Introduction

Only rather recently has the Friedel-Crafts alkylation of alkylaromatics come to be considered a typical electrophilic aromatic substitution. Previously the alkylation reaction was believed to produce atypical isomer distributions. There were three major reasons for this belief.

1. Before the use of infrared and Raman spectroscopy, the methods used for the analysis of alkylaromatic isomers were tedious, unreliable or both. Thus, the propylation of toluene was frequently reported to yield *p*-cymene uncontaminated by *o*- or *m*-cymene.¹ As late as 1954 this claim was made.²

2. Several alkylations were reported in which the proportion of *meta* substitution obtained was anomalously large for an electrophilic reaction.³ Recently, Brown has shown that the substantial proportion of *m*-isopropyltoluene obtained by the propylation of toluene is due to the low selectivity

of the reaction for the activated *ortho* and *para* positions of toluene.⁴

3. An isomer distribution obtained by alkylation can change due to positional isomerization under the Friedel-Crafts reaction conditions. Indeed, since the intermediate σ -complex postulated for alkylation is identical to that postulated for isomerization,⁵ it is questionable that alkylation exclusive of isomerization is possible.

For some time the alkylation of aromatics was believed to involve formation of the alkyl carbonium ion, which then attacked the aromatic ring.^{3a} More recently, evidence has been accumulating which indicates that many alkylations involve displacement by the aromatic ring on the α -carbon of the alkyl derivative catalyst complex.⁶ In contrast to the carbonium ion mechanism, the displacement mechanism implies the possibility

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