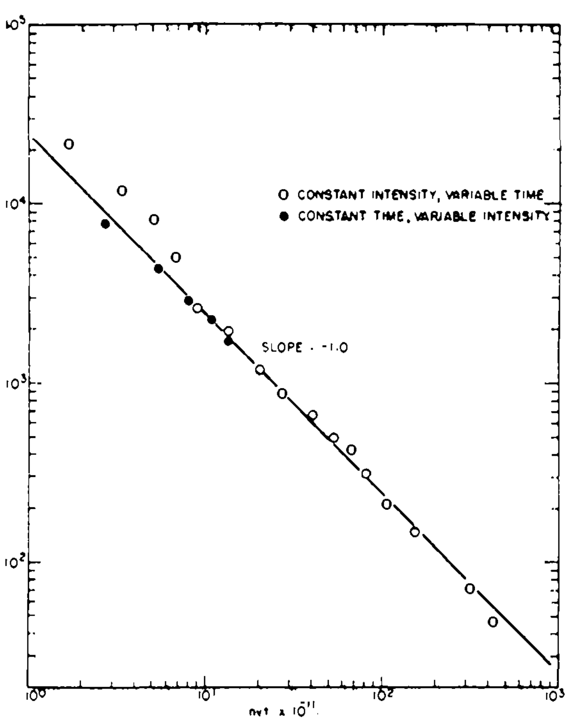

Fig. 2.—Variation of the enrichment of 35.9 h Br^{82} separable from neutron irradiated crystalline KBrO$_3$ with exposure (time expressed as hours).

either by short irradiations, or by the employment of low intensity sources. If an enrichment of 5000 for Br^{82} is found after a one-hour exposure in a slow neutron flux of 6.7×10^{11} n/cm.^{2}/sec., then a value of 5×10^5 might be expected for an intensity of 6.7×10^9 (typical of cyclotron sources) and of 5×10^8 for an intensity of 6.7×10^6 n/cm.^{2}/sec. which is of the order of magnitude of fluxes sustained by Ra + Be neutron sources. Interestingly, although very few data can be found in the literature, the values of 10^7 for the enrichment of P^{32} produced by a recoil reaction with triphenyl phosphate[12] and of 10^8 for I^{128} from ethyl iodide[13] are of this latter order of magnitude. A somewhat smaller enrichment (10^5) than would be expected has been reported in the preparation of 2.59 h Mn^{56} from KMnO$_4$.[14] Despite the high enrichment with weak neutron sources it is emphasized that the specific activity of the separated radioisotope will be independent of the strength of the source.

From the foregoing considerations, the advantage of the Szilard–Chalmers effect should disappear as progressively more intense slow neutron sources become available. However, at present, a quite worthwhile 90-fold enrichment of 35.9 h Br^{82} may be achieved by irradiating pure crystalline KBrO$_3$ for one half-life in a flux of 6.7×10^{11} n./cm.^{2}/sec.

Acknowledgments.—The authors wish to express their sincere thanks to Messrs. P. F. Thomasson and Stanley Rasmussen of the Analytical Division for total bromide analyses on numerous irradiated bromate samples.

[12] O. Erbacher and K. Phillip, *Z. physik. Chem.*, **179A**, 263 (1937).

[13] O. Erbacher and M. Beck, *Z. anorg. Chem.*, **252**, 357 (1944).

[14] U. Drehmann, *Z. physik. Chem.*, **53B**, 327 (1943).

Oak Ridge, Tenn. Received July 16, 1951

[Contribution from the Department of Chemistry, Duquesne University]

The Absorption Spectra of Some Diaryl Ketones, Hydrazones and Azines

By H. Harry Szmant and Clare McGinnis[1]

The comparison of the spectra of a number of diaryl ketones, their hydrazones and azines permits the classification of the observed absorption peaks into the following categories: (1) the peaks which result from the conjugation of the aryl group with the double bond of the carbonyl group, and which are also found in the hydrazones and azines of the ketones. (2) the peaks which result from the resonance which traverses the whole length of the azine molecule; (3) the peaks which correspond to the resonance of the aryl portions of the molecules, or which are traceable to the contributions by individual structural features (*i.e.*, the phenylmercapto- or the phenylsulfonyl groups).

In order that a better understanding may be obtained of the ultraviolet absorption spectra of a series of diaryl ketazines there were also investigated the spectra of the corresponding ketones and hydrazones. Of the diaryl ketazines only that derived from benzophenone seems to have been studied spectrophotometrically.[2] The substituted benzophenone azines are closely related to the recently described azines of substituted acetophenones.[3]

Experimental Results

The hydrazones and azines employed in this study were prepared by the methods developed in this Laboratory.[4] The physical properties and analytical data for the new compounds are listed in Table I. The absorption spectra were determined by means of a Beckman DU spectrophotometer employing solutions in 95% ethanol. The absorption curves are reproduced in Figs. 1–4, and the spectral data are summarized in Table II.

Discussion

The comparison of the spectra of the ketones and the corresponding hydrazones and azines permits the classification of the observed maxima into several groups related to each other from the viewpoint of the probable electronic transitions responsible for their appearance.

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[1] A portion of this material is taken from the M.S. thesis submitted by C. M. to the Faculty of the Graduate School of Duquesne University in June, 1950. Present address of C. M., The Massachusetts Institute of Technology.

[2] E. R. Blout, V. W. Eager and R. M. Gofstein, This Journal, **68**, 1983 (1946).

[3] H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4981 (1950).

[4] H. H. Szmant and C. McGinnis, *ibid.*, **72**, 2890 (1950).

TABLE I

DIARYL KETONE HYDRAZONES AND AZINES

Compound	M.p., °C.[a]	Analyses, %[b] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Thienyl phenyl ketone hydrazone	108–109	65.31	65.37	4.98	4.96
2-Thienyl phenyl ketazine	128–130	70.93	70.69	4.33	3.86
p-Phenylsulfonylbenzophenazine	196–198	71.23	71.20	4.37	4.18
p-Chlorobenzophenazine	148–150	72.73	72.83	4.23	4.04
p,*p*′-Dichlorobenzophenazine	224–225	62.67	62.76	3.24	3.10
2,4′-Dichlorobenzophenone hydrazone	119–121	58.89	58.94	3.80	3.45
2,4′-Dichlorobenzophenazine	165–166	62.67	62.65	3.24	3.21
p-Dimethylaminobenzophenone hydrazone	128–130	75.23	74.93	7.15	7.11
p-Dimethylaminobenzophenazine	194–195	80.68	80.84	6.77	6.84
p-Phenylbenzophenone hydrazone	121–123	83.79	83.76	5.92	5.93
p-Phenylbenzophenazine	168–170	88.68	88.24	5.48	5.12
p-Phenoxybenzophenone hydrazone	86–88	79.14	79.23	5.59	5.47
p-Phenoxybenzophenazine	117–118	83.49	83.52	5.16	4.77
p-Phenylmercaptobenzophenazine	115–116	79.13	78.98	4.89	4.53

[a] All melting points are uncorrected. [b] Microanalyses by Mr. Stragand of the Micro-Analytical Laboratory, University of Pittsburgh.

The first of these may be described as the "aryl ketone" band since it is characteristic of the $C_6H_5C{=}O$ group. Thus the maxima of the ketones investigated here agree closely with those of the corre-

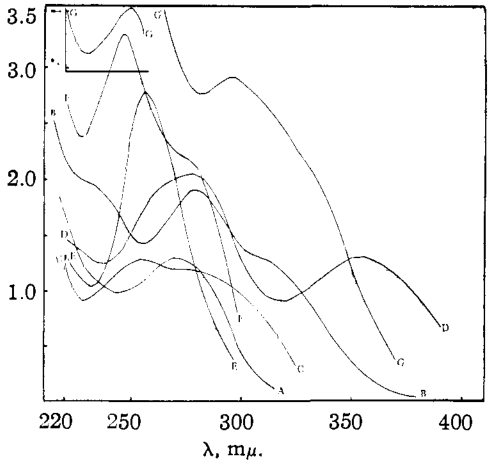


Fig. 1.—Absorption spectra: benzophenone hydrazone (A) and azine (B); 2-thienyl phenyl ketone hydrazone (C) and azine (D); *p*-phenylsulfonyl benzophenone (E), hydrazone (F), and azine (G).

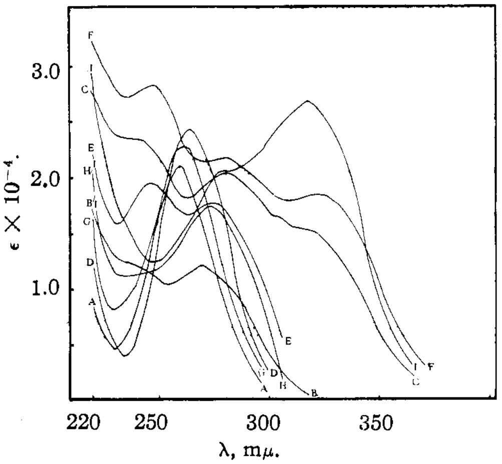


Fig. 3.—Ultraviolet absorption spectra: *p*-chlorobenzophenone (A), -hydrazone (B), and -azine (C); *p*,*p*′-dichlorobenzophenone (D), -hydrazone (E), and -azine (F); 2,4′-dichlorobenzophenone (G), -hydrazone (H), and -azine (I).

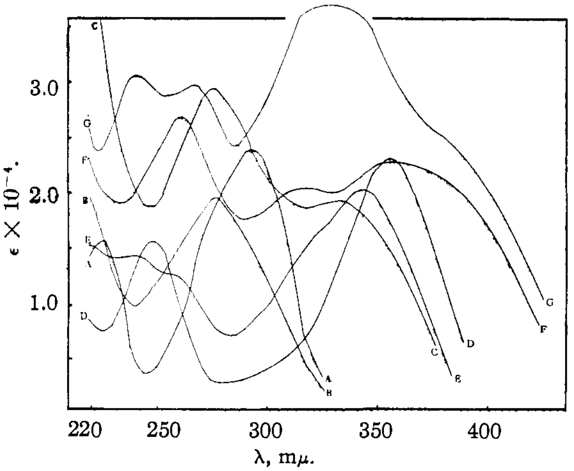


Fig. 2.—Ultraviolet absorption spectra: *p*,*p*′-dimethoxybenzophenone (A), -hydrazone (B), and -azine (C); *p*-dimethylaminobenzophenone (D), -hydrazone (E), and -azine (F); *p*,*p*′-bis-(dimethylamino)-benzophenazine (G).

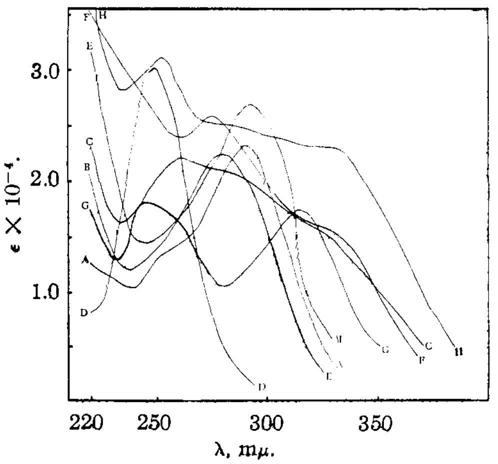


Fig. 4.—Ultraviolet absorption spectra: *p*-phenylbenzophenone (A), -hydrazone (B), and -azine (C); *p*-phenoxybenzophenone (D), -hydrazone (E), and -azine (F); *p*-phenylmercaptobenzophenone (G), and -azine (H).

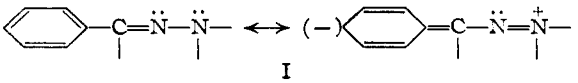
TABLE II

ABSORPTION BANDS OF DIARYL KETONES, HYDRAZONES AND AZINES[a]

Compound	λ_{max},[b] mμ	$\epsilon_{max} \times 10^{-4}$	λ_{max},[c] mμ	$\epsilon'_{max} \times 10^{-4}$	λ''_{max},[d] mμ	$\epsilon''_{max} \times 10^{-4}$
Benzophenone (I)[e]	253	1.86				
hydrazone	270–272	1.30				
azine[f]	277–278	1.89	(310)	1.28	(230)	1.95
2-Thienyl phenyl ketone (II)[g]	263	1.29				
	293	1.33				
hydrazone	255	1.28				
	275	1.20				
azine	276–278	2.03	355	1.28		
p-Phenylsulfonylbenzophenone (III)	257	2.77				
hydrazone	(270)	2.25			245	3.28
azine	247	4.54	295	2.91		
			(310–330)	*ca.* 2.3		
p-Chlorobenzophenone (IV)	260	2.11				
hydrazone	270	1.22			(235)	1.25
azine	280	2.06	(305)	1.65		
			(320)	1.52	(235–245)	2.35
p,*p*′-Dichlorobenzophenone (V)	265	2.44				
hydrazone	275	1.78			247	1.28
azine	281.5	2.14	322–323	1.88	248	2.84
2,4′-Dichlorobenzophenone (VI)	262	2.28				
hydrazine	272	1.75				
azine	(275–285)	2.06	319	2.68		
p,*p*′-Dimethoxybenzophenone (VII)	293	2.40			225	1.59
hydrazone	276–277	1.97			(220)	2.0
azine	276–277	2.94	331–334	1.91	(220)	3.9
p-Dimethylaminobenzophenone (VIII)[h]	355–357	2.28				
	247	1.57				
hydrazone	340–341	2.08			233–234	1.43
	(255)	1.27				
azine	357–358	2.24	315–317	2.04		
	260–263	2.69	(360–400)	*ca.* 2.0		
p,*p*′-Bis-(dimethylamino)-benzophenone (IX)[i]	370	1.9	(390)	2.3		
azine	(320–345)	3.64	(390)	2.3	241	3.06
					266–265	2.98
p-Phenylbenzophenone (X)	291	2.32				
	(253)	1.36				
hydrazone	293	2.72				
azine	262	2.19	(300–330)	*ca.* 1.6		
	(280)	2.10				
p-Phenoxybenzophenone (XI)	249	3.03				
hydrazone	277–281	2.25			(220)	3.2
azine	271	2.61	(320)	1.65	(220)	3.5
p-Phenylmercaptobenzophenone (XII)	315	1.75				
	243	1.85				
azine	(300–315)	2.35	(300–335)	2.35		
	253	3.15			(220)	4.1

[a] Absorption spectra in 95% ethanol. The values in parentheses refer to inflection points, plateaus, shoulders or even regions of unusually high absorption intensity. [b] In this column there are listed the bands which originate presumably from the absorption of the aryl–C=O or the aryl–C=N- chromophores. [c] These bands are assigned to the resonating system which is responsible for the 300 mμ band of benzalazine. [d] In this column there are listed the bands which originate from the absorption of certain portions of the molecules (see Discussion). [e] Jones, THIS JOURNAL, **67**, 2127 (1945). [f] These results are in agreement with those reported in ref. (2). [g] Reference 14. [h] Katzenellenbogen and Branch, *ibid.*, 69, 1615 (1947). [i] Burawoy, *Ber.*, **63**, 3155 (1930).

sponding acetophenones[3] or benzaldehydes. The observed maxima of the hydrazones and certain maxima of the azines are listed in Table II together with "aryl ketone" bands of the parent ketones since it is believed that these maxima are caused by electronic oscillations completely analogous to those taking place in the ketones. In the case of benzophenone hydrazone and azine this band is found in the 270–278 mμ range, and the bathochromic displacement (from the 253 mμ maximum of benzophenone) is at least partially explained by considering the resonance contribution of structures in which the electron flow originates at the nitrogen atom and is directed toward the aromatic ring



I

Contributions from resonance structures of this type in hydrazones and azines explain why electronwithdrawing substituents give relatively large bathochromic effects, and why strong +E substituents cause displacements of the maxima toward *shorter* wave lengths (see column one in Table III). Also, the relative bathochromic effects of the substituents in the ketone and hydrazone series (columns two and three in Table III), and the variations in the difference between the bathochromic effects observed in these two families of compounds (the last column of Table III) can be explained on this basis.

TABLE III

THE EFFECT OF *p*-SUBSTITUENTS ON THE SPECTRA OF KETONES AND HYDRAZONES

Substituent	$\Delta\lambda_{max}$,[a] $m\mu$	$\Delta\lambda'_{max}$,[b] $m\mu$	$\Delta\lambda''_{max}$,[c] $m\mu$	$\Delta\lambda''_{max} - \Delta\lambda'_{max}$, $m\mu$
H[d]	18	...	...	..
Dimethylamino	−16	102	70	−32
Methoxy[d]	−16	40	6	−34
Phenyl	2	38	22	−16
Chloro	5–10	12	1	−11
Phenylsulfonyl	13	4	−1	− 5
Phenoxy	20	−4	8	+12

[a] $\Delta\lambda_{max}$ = (λ_{max} of hydrazone) − (λ_{max} of ketone). [b] $\Delta\lambda'_{max}$ = (λ_{max} of ketone) − (λ_{max} of benzophenone). [c] $\Delta\lambda''_{max}$ = (λ_{max} of hydrazone) − (λ_{max} of benzophenone hydrazone). [d] In agreement with these results are those obtained when the spectra of acetophenone hydrazone (λ_{max} 261.5), *p*-methoxyacetophenone hydrazone (λ_{max} 269), and *p*-hydroxyacetophenone hydrazone (λ_{max} 271) are compared with the maxima of the present ketones (ref. 9). The values in the columns of Table III for these three compounds are (+16, —, —, —); (−7.5, +21, +7.5, −13.5); and (−4, +30.5, +10.5, −20), respectively. The spectra of the acetophenone hydrazones were determined by Mr. Edward Cochran of this Laboratory.

The position of the "aryl ketone" band in the hydrazone and azine derived from benzophenone agrees well with the maxima of the related electronic system of the benzohydryl and trityl ethers of benzophenone oxime (266 $m\mu$ in methylcyclohexane).[5] On the other hand the maxima reported for diaryl ketimines[6] do not show bathochromic displacements with respect to the maxima of the ketones although the double bonded nitrogen group is common to the ketimines and the hydrazones and azines. Thus, it appears that the bathochromic shift is not so much dependent on the nature of the atom linked to the diphenylmethylene group but rather results from the contribution of the resonance phenomenon represented by *I*. It is noteworthy that the maximum of 1,1-diphenylethylene (250 $m\mu$)[7] also coincides with that of benzophenone.

The second of the characteristic absorption bands in this group of compounds is observed in the case of the azines and is related to the 300 $m\mu$ maximum of benzalazine. This absorption peak is generally agreed to result from the electronic oscillations traversing the whole length of the aryl azine molecule.[2,3] In the parent compound, benzophenazine, this absorption appears only in the form of an inflection point at about 310 $m\mu$, but in most of the substituted benzophenone azines there are found prominent maxima. Several of the azines studied here show a remarkable agreement in the position of this band with those reported for the corresponding substituted benzalazines. Thus, the maximum of *p*-chlorobenzalazine (322 $m\mu$)[8] is recognized in the spectra of the three chloro-substituted benzophenone azines, and the same is true of the maxima of *p*-methoxybenzalazine (331 $m\mu$),[8] and *p*-dimethylaminobenzalazine (400 $m\mu$).[8] Whenever we deal with an azine derived from an unsymmetrical ketone there are possible as many as three different electronic oscillations traversing the azine molecule. Even if only two make significant contributions to the excited states it is probable that the long wave lengths maxima are not distinct and may appear in the form of inflection points. Thus, *p*-phenylsulfonylbenzophenone azine has a maximum at 295 $m\mu$ but also shows very strong absorption in the 310–330 $m\mu$ range. Also, *p*-chlorobenzophenone azine has two inflection points at approximately 305 and 320 $m\mu$, and *p*-dimethylaminobenzophenone azine has in addition to a maximum at 315–317 $m\mu$ also a broad shoulder extending over the range of 360–400 $m\mu$. For the same reason the spectra of the azines of *p*-phenyl-, *p*-phenoxy- and *p*-phenylmercaptobenzophenones all exhibit either inflection points or broad shoulders stretching into the near ultraviolet range.

In addition to these two characteristic bands there appear also additional absorption peaks which can be identified to belong to certain portions of the molecular system. Thus, the hydrazones and azines of the chloro-substituted benzophenones exhibit minor bands in the 235–248 $m\mu$ region which appear to correspond to the "second primary band" of Doub and Vandenbelt.[9] The same seems to be true of the 225 $m\mu$ peak of *p,p'*-dimethoxybenzophenone and the high intensity absorption of the corresponding hydrazone and azine in the 220 $m\mu$ region of the spectrum. The minor absorption bands found in the dimethylamino-substituted compounds have their counterpart in the 241–243 $m\mu$ peaks reported by Kumler[10] for the *p*-substituted benzaldehyde and acetophenone. The characteristic plateau of the biphenyl system[3,11] appears again in the *p*-phenyl-substituted compounds reported here, particularly in the benzophenone and in the azine. In the case of the latter compound this band seems to fuse with those expected of the azine chromophore so that a broad band stretching over some 100 $m\mu$ results. The fact that while the absorption of the hydrazone drops rapidly beyond 310 $m\mu$ while that of the azine continues at a high level to almost 350 $m\mu$ indicates the presence of the benzalazine band in the *p*-phenyl compound.

The typical absorption peak of the phenylmercapto group at approximately 250 $m\mu$[12] is apparent in the spectra of the *p*-phenylmercapto-substituted ketone and azine. In the azine the fusion of the two above mentioned characteristic bands results in a broad shoulder extending to approximately 330 $m\mu$.

p-Phenylsulfonylbenzophenone exhibits a remarkably simple absorption curve with a maximum at 257 $m\mu$. The simplicity of this curve probably

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[5] A. C. Cope and A. C. Haven, Jr., THIS JOURNAL, **72**, 4898 (1950).

[6] P. L. Pickard and D. J. Vaughan, *ibid.*, **72**, 5017 (1950).

[7] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2017 (1950).

[8] H. C. Barany, E. A. Braude and M. Pianka, *ibid.*, 1898 (1949).

[9] L. Doub and J. M. Vandenbelt, THIS JOURNAL, **69**, 2714 (1947).

[10] W. D. Kumler, *ibid.*, **68**, 1184 (1946).

[11] H. H. Szmant and H. J. Planinsek, *ibid.*, **72**, 4042 (1950).

[12] See ref. 3, and the references cited there.

results from the fact that both the benzoyl and phenylsulfonyl groups have their maximal absorptions at about this position[13] and in this particular structure the two chromophores show little interaction. The spectrum of the corresponding hydrazone is more complex since in addition to the maximum at 245 mμ there is also apparent an inflection point at about 270 mμ. The corresponding azine has an extremely strong absorption peak at 247 mμ (ε 45,500) which is almost equivalent to a double hydrazone peak, but there is also present a second peak at 295 mμ. The breadth and intensity of this secondary peak, suggests the presence of a masked absorption band at about 320 mμ which could be attributed to the typical benzalazine absorption.

While the spectrum of 2-thienyl phenyl ketone has two well-defined maxima at 263 and 295 mμ,[14] there are found in the spectrum of the corresponding hydrazone two similar bands, but they overlap to a great extent. The absorption curve of the corresponding azine is of great interest since it presents two distinct bands at 277 and 353 mμ. The first of these bands resembles closely the 277 mμ band of the azine of benzophenone and the 265 mμ band of the azine of 2-thienyl methyl ketone.[3] The second band, however, differs in position from the benzalazine band in benzophenone azine (*ca.* 310 mμ) and also the 335 mμ band of the azine of 2-thienyl methyl ketone.[3] The large difference in the maxima of these two thiophene ketazines suggests that the chromophoric system in the azine of 2-thienyl phenyl ketone contains one thiophene and one benzene ring each.

Acknowledgment.—We wish to acknowledge the aid of the Research Corporation in defraying a part of the cost of this project.

PITTSBURGH 19, PENNA. RECEIVED JUNE 18, 1951

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(13) The absorption spectra of various sulfones have been recently studied by Fehnel and Carmack (THIS JOURNAL, **71**, 231 (1949); **72**, 1292 (1950)); and Koch (*J. Chem. Soc.*, 408 (1949)).

(14) H. H. Szmant and A. J. Basso, THIS JOURNAL, **73**, 4251 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Action of Aluminum Bromide on Benzyl Phenyl Ether

BY D. STANLEY TARBELL AND JOHN C. PETROPOULOS

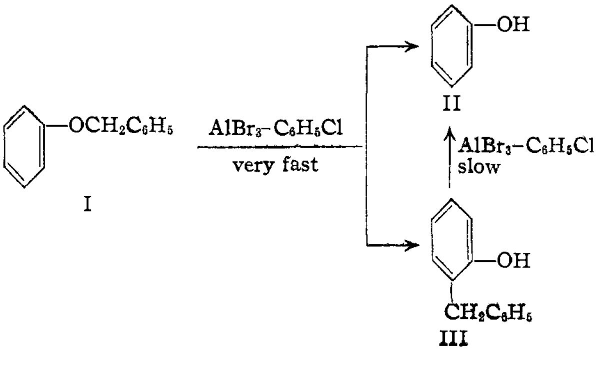
Benzyl phenyl ether has been found to be converted very rapidly by aluminum bromide in chlorobenzene solution to a mixture of about 40% phenol, 55% *o*-benzylphenol and dichlorodiphenylmethane. The ratio of the phenolic products is the same at −40° as at 25°, and is unaffected by the use of benzene or nitrobenzene as solvent. The *o*-benzylphenol produced in the initial rapid reaction is converted to phenol at a slower measurable rate, the first order rate constant of which is identical with the rate constant obtained from pure *o*-benzylphenol under the same conditions. *p*-Benzylphenol has been shown not to be an intermediate in the rapid formation of phenol from benzyl phenyl ether. The *o*-benzylphenol is believed to be formed from the ether by an intramolecular process, and the contrast between the action of the aluminum bromide on benzyl phenyl ether and the corresponding sulfide (previously studied) is discussed. The dichlorodiphenylmethane, formed in chlorobenzene from aluminum bromide and benzyl phenyl ether or benzyl bromide, is shown to be a mixture of roughly equivalent amounts of 3,3′- and 3,4′-dichlorodiphenylmethane.

We have studied the reaction between benzyl phenyl ether (BPE) and aluminum bromide, in order to compare the action of this strong Lewis acid on the oxygen ether with its action on the sulfur analog, benzyl phenyl sulfide.[1]

In the initial experiments, the rate of formation of phenol from BPE by aluminum bromide in chlorobenzene solution was followed; the phenol was extracted from a mixture of chlorobenzene–ethyl ether with 20% alkali, after quenching the reaction, and was determined by the bromate method.[2] By this procedure, there was observed an extremely rapid formation of about 40% of phenol, followed by slower measurable increase in the amount of phenol, until phenol formation was virtually complete. This unusual behavior was eventually traced to the fact that there was an initial very rapid reaction to form about 40% phenol (II) and about 55% of *o*-benzylphenol (III); the latter was not extracted by alkali under the conditions mentioned above, and hence had not been determined. By a slight change in the procedure, it was possible to determine both phenol and *o*-benzylphenol in the same solution.

It was shown that the slow production of phenol was due to conversion of *o*-benzylphenol to phenol, with transfer of the benzyl group to the solvent. The scheme shown below was established by isolation experiments, in which BPE and aluminum bromide in chlorobenzene were mixed under conditions comparable to those used in the rate runs; the reaction was quenched within a few seconds, phenol (II) and *o*-benzylphenol (III) were isolated, and were identified by comparison of crystalline derivatives of authentic samples.

The possibility that the initial rapid formation of phenol occurred through *p*-benzylphenol as intermediate was ruled out by showing that, al-



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(1) (a) Harnish and Tarbell, THIS JOURNAL, **70**, 4123 (1948); (b) Wilson and Tarbell, *ibid.*, **72**, 5200 (1950).

(2) Redman, Weith and Brock, *Ind. Eng. Chem.*, **5**, 389 (1913); Day and Taggart, *ibid.*, **20**, 545 (1928).