Similar experiments after oxidation with sodium bismuthate for 5 min. at 60° in 5 M nitric acid also showed less than 10% carrying on zirconium phosphate and greater than 80% carrying on lanthanum fluoride from the supernatant made 3 M in hydrochloric acid and 1 M in hydrofluoric acid.

Although there are uncertainties in the tracer experiments, due largely to the small amount of californium available, it can be concluded that the oxidation of Cf(III) to the (IV) or (VI) states in aqueous solution even with these strong oxidizing agents is not possible or that the oxidation is slow.

Discussion

The chemical properties of californium all indicate that it fits in well as the ninth actinide element. Perhaps the best evidence for this is a comparison of the relative rates of elution with ammonium citrate of the actinide elements californium–berkelium–curium–americium and their rare earth homologs dysprosium–terbium–gadolinium–europium. To facilitate this comparison the elution data for the rare earths and actinides are plotted together in Fig. 2. Here the ordinates are normalized to show equal amounts of activity. The relative spacing for californium, berkelium, curium and americium were taken from Fig. 1 and from an elution experiment in which berkelium, curium and americium were present. The curves for the rare earths were taken from the previously mentioned sources.

A remarkable analogy between these two groups of elements is apparent, indicating that the same sequence of changes in ionic radius is encountered on filling in the 5f electrons as occurs on filling the 4f shell. It seems quite clear that curium represents the midway point in the actinide transition series of elements in view of its position analogous to gadolinium. The most obvious difference between the two groups is the larger magnitude of the contraction found in the actinides. That this should be the case is quite reasonable when one considers that the more loosely bound 5f electrons of the actinides would certainly be less effective as shielding electrons.

The experiments with respect to oxidation of californium above the (III) state are incomplete and further work is necessary in order to establish whether such states can exist in aqueous solution. The difficulty of oxidizing berkelium to the (IV) state[4] indicates that such higher oxidation states may not be expected. However, as the second element beyond the midpoint of this transition series, the possibility of oxidation to a (V) state (CfO_2^+) must be borne in mind, particularly in view of the great stabilizing influence of the two oxygen atoms found in these elements for the MO_2^+ (and MO_2^{++}) type of ions.

Acknowledgment.—It is a pleasure to acknowledge the help and advice of A. Ghiorso, G. H. Higgins and E. K. Hulet. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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RECEIVED AUGUST 4, 1950

The Schmidt Reaction of Some *p*-Substituted Acetophenones

BY H. H. SZMANT AND J. J. MCINTOSH

In connection with another study, we had the opportunity to investigate the Schmidt reaction of a number of *p*-substituted acetophenones. In view of the current interest in the mechanism of the reactions of hydrazoic acid with ketones,[1-8] and in view of the fact that few reactions of this type involving acetophenones containing electron withdrawing substituents are recorded in the literature, we wish to report our results at this time.

Experimental

It was hoped that a uniform procedure could be employed for all the compounds in this study, and a medium of acetic acid containing sulfuric acid catalyst was thus chosen (Procedure A). However, several compounds were recovered unchanged when subjected to the Schmidt reaction in the above mentioned medium, and in those cases a medium of higher acid strength was employed (Procedure B).

Procedure A.—The ketone, 0.05 mole, was dissolved in 30–50 cc. of glacial acetic acid containing 0.1 mole of concentrated sulfuric acid. To the stirred solution at 60–70° there was then added sodium azide (0.075 mole) in small portions at such a rate that the temperature did not rise above 70°. The mixture was stirred with heating until all the evolution of nitrogen subsided (2–6 hours), and was then allowed to stand overnight at room temperature. The reaction mixture was poured onto ice and the solid product was filtered off, washed with water, dried and its melting point was determined. Whenever the melting point of the crude product was relatively close to that reported for the substituted acetanilide, the product was simply purified by crystallization and in most cases the purified acetanilide was also hydrolyzed to the corresponding aniline. When, on the other hand, the melting point differed appreciably from the literature value, the crude product was hydrolyzed and an attempt was made to isolate the substituted benzoic acid or aniline by conventional means.

Procedure B.—This procedure differed from the above in that the reaction was carried out in 50 ml. of concentrated sulfuric acid, and the reaction temperature was lowered to 30°.

The results obtained in this study are summarized in Table I.

Discussion

It is generally agreed that the Schmidt reaction of ketones is acid catalyzed, and the results of this study offer further evidence on this point. In the case of substituted acetophenones in which the electron withdrawing character of the substituents caused a decrease in the basicity of the carbonyl oxygen atom, the reaction failed when only a catalytic amount of sulfuric acid was employed in the acetic acid medium. The reaction, how-

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(1) Sanford, Blair, Arroya and Sherk, THIS JOURNAL, **67**, 1942 (1945).

(2) Smith, *ibid.*, **70**, 320 (1948).

(3) Newman and Gildenhorn, *ibid.*, **70**, 317 (1948).

(4) Smith and Horwitz, *ibid.*, **72**, 3718 (1950).

(5) Shechter and Kirk, Abstracts of Papers, 117th Meeting of the American Chemical Society, Philadelphia, 1950, p. 49L.

(6) Wolff, in Adams, "Organic Reactions," v. III, John Wiley and Sons, New York, N. Y., 1946, p. 307.

(7) Dice and Smith, *J. Org. Chem.*, **14**, 179 (1949).

(8) Alexander, "Ionic Organic Reactions," John Wiley and Sons, New York, N. Y., 1950, p. 71.

TABLE I

THE SCHMIDT REACTION OF SOME SUBSTITUTED ACETOPHENONES

No.	p-$\mathrm{RC_6H_4COCH_3}$ R =	Procedure	Crude yield, %	Product m. p., °C.[a]	p-$\mathrm{RC_6H_4NHCOCH_3}$ M. p., °C. (lit.)	p-$\mathrm{RC_6H_4NH_2}$ M. p., °C. (lit.)
1	H	A	99	110–112	113 (113)[b]	.....
2	$\mathrm{C_6H_5}$	A	99	168–169	170–171 (171)[b]	51–52 (53)[b]
3	$\mathrm{C_6H_5CH_2}$	A	70	117–200	...[c] (135)[b]	214–215[c] (214–216)[c]
4	$\mathrm{C_6H_5O}$	A	99	123–126	126–127 (127)[b]	84 (84–85)[b]
5	$\mathrm{C_6H_5S}$[d]	A	99	137–142	144–146 (146)[b]	96 (93–96)[b]
6	$\mathrm{C_6H_5SO}$[d]	[e]	60	130–135	137–137.5 (137)[f]	151 (151)[g]
7	$\mathrm{C_6H_5SO_2}$[d]	B	85	177–187	188–189 (195)[h]	172–174 (176)[h]
8	$\mathrm{O_2N}$	B	70[i]	144–146	...[i] (215)[j]	146–147 (147)[b]
9	p-$\mathrm{O_2NC_6H_4}$	A	80[k]	180–190	...[k] (264)[l]	198 (198)[l]
10	p-$\mathrm{O_2NC_6H_4O}$	B	50	144–145	145 (145)[m]	.....

[a] All melting points are uncorrected. [b] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943. [c] The crude product was hydrolyzed with dilute acid and the *p*-benzylaniline was isolated in 60% yield as the hydrochloride (Basler (*Ber.*, **16**, 2718 (1884)) reports m. p. 214–216°). The residue from the acid hydrolysis gave on alkaline hydrolysis 0.1 g. (1%) of *p*-benzylbenzoic acid melting at 155–157° (lit.[b] m. p. 155–157°). [d] Szmant and Palopoli, THIS JOURNAL, **72**, 1757 (1950). [e] Solvent trichloroacetic acid (refs. 2, 7). [f] Identical with the product obtained by the oxidation of *p*-phenylmercaptoacetanilide (Szmant and McIntosh, unpublished data.) [g] Northey, "The Sulfonamides and Allied Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 385. [h] Ref. [g], p. 364. [i] The product was found to hydrolyze when the reaction mixture was poured on ice and allowed to stand overnight. No *p*-nitrobenzoic acid was detected. [j] Kaufmann, *Ber.*, **42**, 3481 (1909). [k] Hydrolysis occurred on quenching the reaction mixture in water and allowing the mixture to stand overnight. No *p*-(4-nitrophenyl)-benzoic acid could be isolated. [l] Willstätter and Kalb, *Ber.*, **39**, 3479 (1906). [m] Szmant and McIntosh, unpublished data.

ever, proceeded satisfactorily in a concentrated sulfuric acid medium except in the case of *p*-phenylthionylacetophenone (compound 6).

Since even catalytic amounts of sulfuric acid caused a decomposition of this sulfoxide, the reaction was attempted using glacial acetic acid at 80°, and glacial acetic acid containing trichloroacetic acid. Under these conditions of weak acidity, the sulfoxide was not decomposed but the Schmidt reaction also failed. A satisfactory medium of proper range in acidity was found in trichloroacetic acid.[2,7]

In connection with the mechanism of the Schmidt reaction it is noteworthy that the isolated products in all cases indicate that the migration of the aryl group took place in preference to the methyl group regardless of whether electron withdrawing or electron donating substituents were present on the benzene ring of the acetophenone.

The product of the migration of the methyl group was isolated in only one case, namely, with *p*-benzylacetophenone. The crude reaction product of this ketone was hydrolyzed in an acid medium and gave a 60% yield of *p*-benzylaniline. The residue of the hydrolysis was then subjected to an alkaline hydrolysis and a small amount of *p*-benzylbenzoic acid was thus isolated. In view of the considerable difficulty with which benzamides are hydrolyzed under acidic conditions, it is possible that the minor amounts of the products obtained by the migration of the methyl group were overlooked.

The results obtained in this study support the previously enunciated conclusions that the migration of groups in the Schmidt reaction of unsymmetrical ketones is controlled primarily by steric factors.[4,6,7,8]

Acknowledgment.—We acknowledge with thanks the interest of Dr. Harold Shechter, of the Ohio State University, and the financial aid of the Research Corporation.

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RECEIVED MAY 26, 1950

The Molecular Size and Shape of Yeast Ribosenucleic Acid

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There have been few studies on the molecular shape of yeast ribosenucleic acid (YNA). We have been able to estimate both the molecular size and shape of YNA by combining its diffusion constant ($D_{20,w}$) with volume fraction intrinsic viscosity ($[\eta]_V$).

Diffusion constants were determined refractometrically in phosphate buffer (*p*H 7.7, ionic strength 0.2) by the Svensson schlieren method[1] using the Neurath-type diffusion cell.[2] Viscosity measurements were carried out at 20.0° on the solutions of various concentrations in the same phosphate buffer.

Representative results are shown in Table I.

TABLE I

YNA	Diffusion constant $D_{20,w} \times 10^7$ cm.^{2}/sec.	Intrinsic viscosity $[\eta]_V$	Partial sp. volume V_{20}
I	5.75	30.3	0.59
II	7.04	19.0	.59
II′	6.5	17.0	.58

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(1) H. Svensson, *Kolloid-Z.*, **87**, 181 (1939).

(2) H. Neurath, *Science*, **93**, 431 (1941).