TABLE I

THE SCHMIDT REACTION OF SOME SUBSTITUTED ACETOPHENONES

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 [f] Identical with the product obtained by the oxidation of *p*-phenylmercaptoacetanilide (Szmant and McIntosh, unpublished data.)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 [m] Szmant and McIntosh, unpublished data.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

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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).

TABLE II

YNA	Flattened ellipsoid					Elongated ellipsoid				
	a/b	f/f_0	M	a(Å.)	b(Å.)	b/a	f/f_0	M	a(Å.)	b(Å.)
I	43.0	2.26	19,000	115	2.7	17.2	1.88	33,000	15	262
II	26.2	1.94	17,000	93	3.6	12.7	1.68	25,000	15	196
II′	23.2	1.87	23,000	99	4.3	11.8	1.64	35,000	17	207

YNA-I is the sample prepared from the fresh bakers' yeast ("Oriental" Yeast Co., Tokyo) by the method of Clarke and Schryver.[3] A trace of protein impurity can be further removed by shaking with chloroform–amyl alcohol mixture according to the method of Sevag.[4] These protein-free samples, YNA-II and -II′, contain 8.90 and 9.01% phosphorus, respectively. The diffusion constant obtained by us is far smaller than that found by previous investigators[5] and corresponds to a molecular weight of 120,000–220,000 when YNA is assumed to be an unhydrated sphere.

We have tried to explain the large value of intrinsic viscosity by assuming the molecule of YNA is either a hydrated sphere or an ellipsoid of revolution. In the former case, however, the hydration becomes unreasonably large, *i.e.*, 6.6, 3.9 and 3.4 g. of water per one gram of nucleic acid for YNA-I, -II and -II′, respectively. Therefore, the molecule of YNA must be ellipsoidal.

In the latter case, the axial ratio (a/b or b/a) of an ellipsoid of revolution considered to be a model of YNA molecules can be evaluated from the volume fraction intrinsic viscosity by the Simha equation.[6] From this axial ratio, Svedberg's frictional ratio (f/f_0) can be calculated by using the equation derived by Perrin[7] and by Herzog, Illig and Kudar.[8] With this frictional ratio, diffusion constant and partial specific volume, the molecular weight (M), the length of axis of revolution (b) and the length of equatorial axis (a) of ellipsoid of revolution can easily be evaluated. In Table II are shown these values.

From these results, it seems impossible to consider YNA as a flattened molecule, for its thickness (b) is found to be far too small (not greater than about 4 Å.). The data appear to be more consistent with the concept of an elongated molecule. It is very interesting in this case to find that the diameter of YNA molecule (a) is about 15–17 Å. and is quite identical with that of thymonucleic acid[9] and of the pentosenucleic acid of tobacco mosaic virus.[10]

It might be, therefore, reasonable at the present time to conclude that the shape of a YNA molecule is essentially rod-like, *i.e.*, 15–17 Å. in diameter and 200–260 Å. long, and its molecular weight is at least about 30,000.

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[3] G. Clarke and S. B. Schryver, *Biochem. J.*, **11**, 319 (1917).

[4] M. G. Sevag, *Biochem. Z.*, **273**, 419 (1934).

[5] H. S. Loring, *J. Biol. Chem.*, **128**, Proceedings lxi (1939); W. E. Fletcher, J. M. Gulland, D. O. Jordan and H. E. Dibben, *J. Chem. Soc.*, 30 (1944); G. Schramm, G. Bergold and H. Flammersfeld, *Z. Naturforsch.*, **1**, 328 (1946).

[6] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

[7] F. Perrin, *J. Phys. Rad.*, **7**, 1 (1936).

[8] R. O. Herzog, R. Illig and H. Kudar, *Z. physik. Chem.*, **A167**, 329 (1933).

[9] H. G. Tennent and C. F. Vilbrandt, THIS JOURNAL, **65**, 424 (1943); H. Kahler, *J. Phys. Colloid Chem.*, **52**, 676 (1948).

[10] S. S. Cohen and W. M. Stanley, *J. Biol. Chem.*, **144**, 589 (1942).

COMMUNICATIONS TO THE EDITOR

STRUCTURAL FEATURES OF AN ACID OF THE PHTHIOIC TYPE[1]

Sir:

Phthioic acid, the physiologically active fraction isolated from tubercle bacillus,[2] has been described as 3,13,19-trimethyl-tricosanoic acid,[3] but this structure has been shown untenable.[4] A continuation of the study of this interesting material has become possible through the generosity of Prof. R. J. Anderson, who has supplied us with 24 g. of a crude methyl phthioate fraction. Fractionation and systematic refractionation of this material through a four-foot column of the Podbielniak type has yielded 39 fractions, whose rotations and indices of refraction indicate the presence of at least eleven components. About one-fourth of the total appeared to be one component, and four successive fractions showed the same boiling point, optical rotation and index of refraction; b. p. 232.0° (2.0 mm), $[\alpha]^{25}\mathrm{D} + 14.7°$, $n^{25}\mathrm{D}$ 1.4600. Saponification yielded a polymorphic acid whose rotation was not significantly changed by recrystallization from acetone; m.p. 26–27° and 38–41°, $[\alpha]^{25}\mathrm{D} + 17.8°$, $n^{25}\mathrm{D}$ 1.4666. *Anal.* Calcd. for $C_{28}H_{54}O_2$: C, 79.55; H, 12.88; eq. wt., 422.7. Found: C, 79.18; H, 12.56; eq. wt., 423.7, 426.8. Analysis for terminal methyl

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[1] This investigation was supported in part by a research grant from the National Institute of Health, Public Health Service.

[2] M. A. Spielman and R. J. Anderson, *J. Biol. Chem.*, **112**, 759 (1936).

[3] N. Polgar and R. Robinson, *J. Chem. Soc.*, 389 (1945).

[4] J. Cason and F. S. Prout, THIS JOURNAL, **70**, 879 (1948).