***cis*-2-Methylcyclopentanol.**—The 2-methylcyclopentanol obtained by reduction of 2-methylcyclopentanone with sodium and ether was converted to the *p*-toluenesulfonate by the general method of Tipson[20] except that the reaction mixture was kept at 0° for three hours. The *p*-toluenesulfonate was recrystallized to constant melting point from 30–60° petroleum ether[21]; *ca.* 42% yields of *trans*-2-methylcyclopentyl *p*-toluenesulfonate melting at 33.8–34.5° (lit.[11a] 34.4°) were obtained.

A mixture of 25.4 g. (0.10 mole) of *trans*-2-methylcyclopentyl *p*-toluenesulfonate, 10.9 g. (0.11 mole) of freshly fused potassium acetate and 117 ml. of acetic anhydride free of acetic acid[22] was heated in an oil-bath at 90–100° under reflux with stirring for 48 hours. It was then cooled and added to 3880 ml. of 2.5 *N* sodium hydroxide. After refluxing for one hour with stirring the alcohol was removed by azeotropic distillation with water. About 3 l. of distillate was collected. The distillate was saturated with potassium carbonate and extracted with ether. The ether extracts were dried over potassium carbonate, the ether was removed through a short Vigreux column and the *cis*-2-methylcyclopentanol was distilled. A 22% yield of material boiling at *ca.* 68° (55 mm.) was obtained.

This material was purified by conversion to the 3,5-dinitrobenzoate, recrystallization to constant melting point, reduction with lithium aluminum hydride and fractionation as described above for *trans*-2-methylcyclopentanol. *cis*-2-Methylcyclopentanol boiled at *ca.* 75° (45 mm.), n^{25}_{D} 1.4533, d^{25}_{4} 0.9267; *MR* calcd. 29.24, *MR* found 29.23.

Anal. Calcd. for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: C, 71.74; H, 11.99.

The **p-nitrobenzoate** melted at 48.7–49.0° (lit.[11a] 52.5°). Addition of 5 and 21% *trans*-2-methylcyclopentyl *p*-nitrobenzoate lowered the melting point only 0.5 and 0.2°, respectively; addition of 51% raised it to 52.6–53.6°.

The **3,5-dinitrobenzoate** melted at 85.8–86.0° (lit. 67.7°,[11a] 66–67°[11b]).

Anal. Calcd. for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.90. Found: C, 53.15; H, 4.69.

The **p-toluenesulfonate** melted at 26–27° (lit.[11a] 14.2°). It decomposed before it could be analyzed.

cis-2-Methylcyclopentanol was oxidized to 2-methylcyclopentanone with chromic acid according to the procedure of Mosher and Langerak[23] except that the reaction mixture was allowed to stand overnight at room temperature and the product was isolated by extraction with ether. The 2,4-dinitrophenylhydrazone melted at 156.6–157.0°. A mixture of this derivative and the 2,4-dinitrophenylhydrazone of 2-methylcyclopentanone, m.p. 159.0–159.4°, melted at 157.0–157.6°. The semicarbazone melted at 172.8–174.3°. A mixture of this material and authentic 2-methylcyclopentanone semicarbazone, m.p. 175.4–176.2°, melted at 174.8–175.9°.

Analysis of Mixtures of *cis*- and *trans*-2-Methylcyclopentanol.—Determination of the isomeric composition of mixtures of *cis*- and *trans*-2-methylcyclopentanol was carried out by converting the samples to the 3,5-dinitrobenzoate derivatives and determining the composition of the derivatives from the binary melting point diagram. Data used in constructing the melting point diagram are shown in Table I.

TABLE I

THE MELTING POINTS OF MIXTURES OF *cis*- AND *trans*-2-METHYLCYCLOPENTYL 3,5-DINITROBENZOATES

% *cis*	M.p., °C.	% *cis*	M.p., °C.
0.0	86.0–87.0	63.3	69.3–71.5
11.2	81.2–82.4	75.1	73.3–75.8
26.1	74.8–77.2	93.1	82.1–83.6
37.1	70.4–72.7	100.0	85.8–86.0
49.2	65.2–66.3		

Synthetic mixtures of *cis*- and *trans*-2-methylcyclopentanol containing 14.0, 32.8 and 59.9% *cis* gave 3,5-dinitrobenzoates melting at 81.0–81.9°, 73.8–75.2°, and 68.8–70.2°, respectively, indicating that they contained 13, 30 and 62% *cis*-2-methylcyclopentanol.

The melting point of the 3,5-dinitrobenzoate melting at 65.2–67.8° was raised by the addition of a small amount of *cis*-3,5-dinitrobenzoate and lowered by the addition of a small amount of *trans*-3,5-dinitrobenzoate; therefore this material is 58% *cis*.

Lithium Aluminum Hydride Reduction of 2-Methylcyclopentanone.—2-Methylcyclopentanone, which had been purified by fractionation with a Holzmann column, b.p. 137.5° (761 mm.), n^{25}_{D} 1.4341 (lit.[16] n^{20}_{D} 1.4347), was reduced with lithium aluminum hydride according to the procedure of Roberts and Sauer.[24] The metal alcoholate was decomposed with water as described above for the reduction of *trans*-2-methylcyclopentyl 3,5-dinitrobenzoate. The product was found to contain 25% of the *cis* isomer: the 3,5-dinitrobenzoate melted at 76.0–77.4° and the melting point was lowered by the addition of *cis*-3,5-dinitrobenzoate and raised by the addition of *trans*-3,5-dinitrobenzoate. When the reaction mixture was refluxed for ten hours the composition of the product was the same.

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[20] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[21] After seed crystals were available crystallization occurred readily at 0°.

[22] W. S. Calcott, F. L. English and O. C. Wilbur, *Ind. Eng. Chem.*, **17**, 942 (1925).

[23] W. A. Mosher and E. O. Langerak, THIS JOURNAL, **71**, 286 (1949).

[24] J. D. Roberts and C. N. Sauer, *ibid.*, **71**, 3925 (1949).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organic Compounds of Uranium. I. 1,3-Dicarbonyl Chelates

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This is the first paper in a series concerned with volatile compounds of uranium. Twenty-seven uranium(IV) 1,3-dicarbonyl chelates and 14 uranyl 1,3-dicarbonyl chelates are described.

In 1941, work was undertaken in this Laboratory toward finding compounds of uranium suitable for isotope separation.[1] Of particular interest were substances of high volatility, high stability and low molecular weight. Since the known chemistry of uranium at that time was confined almost entirely to inorganic derivatives, our approach to the problem was to prepare and study new organic uranium compounds. Some prior work in this Laboratory had already indicated that simple organometallic derivatives like tetramethyluranium, if they existed at all, were extremely unstable, and their isolation offered little chance of success. Therefore, attention was directed toward the preparation of other types of organic compounds linked to uranium

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[1] This work was undertaken at the request of the Office of Scientific Research and Development. We are indebted to the Atomic Energy Commission for permission to publish these results.

TABLE I

URANIUM(IV) DICARBONYL COMPOUNDS

$U(RCOCHCOR')_4$

R	R	Reference diketone	Yield, %	M.p., °C.	B.p. °C.	B.p. Mm.	Uranium, % Calcd.	Uranium, % Found
CH_3	CH_3[a,b]	[d]	85	173	Dec. on distn.		37.6	37.8
CH_3	C_2H_5[b]	[d]	50	63	142	0.0002	34.5	34.5
CH_3	C_3H_7	[d]	58	Liq.	158	.001	31.9	31.9
CH_3	$CH(CH_3)_2$[b]	[d]	54	Liq.	155	.001	31.9	31.5
CH_3	C_4H_9	[d]	48	Liq.	175	.001	29.7	29.7
CH_3	$C(CH_3)_3$[b]	[d]	62	Liq.	158	.002	29.7	29.5
CH_3	C_5H_{11}	[d]	32	Liq.	180	.0001	27.7	27.8
CH_3	C_6H_{13}	[d]		Liq.	Dec. on distn.			
CH_3	C_4H_3O[b,c]	[d]	20	225			28.2	27.7
CH_3	C_6H_5[b]	[d]	74	206 d.			27.0	27.7
CH_3	$CH_2OC_2H_5$	[d]	12	80	Dec. on distn.		29.4	29.8
C_2H_5	C_2H_5[b]	[d]	45	63	145	.0002	31.6	31.6
C_3H_7	C_3H_7	[d]	75	21	170	.0003	27.7	27.6
C_6H_5	C_6H_5	[d]		168				
CF_3	CH_3[b]	[e]	88	146			28.1	28.6
CF_3	C_2H_5	[f]	74	60	116	.001	26.3	26.3
CF_3	C_3H_7		88	15	132	.001	24.7	24.7
CF_3	$CH(CH_3)_2$		86	78	134	.003	24.7	24.7
CF_3	C_4H_9		91	Liq.	142	.005	23.4	23.2
CF_3	$CH_2CH(CH_3)_2$	[f]	88	82	141	.002	23.4	23.3
CF_3	$C(CH_3)_3$[b]	[h]	74	136	145	.0002	23.4	23.4
CF_3	C_5H_{11}			Liq.	166	.004	22.1	22.5
CF_3	C_6H_5	[f]			191	.003	20.7	20.7
CF_3	OCH_3		51	90	114	.0002	26.0	26.1
CF_3	OC_2H_5[b]	[i]	83	65	123	.0008	24.5	24.6
CF_3	OC_4H_9		65	Liq.	162	.008	22.0	21.4
CF_3	CF_3	[e,g]	29	60	70	.001	22.4	22.3

[a] Previously prepared by W. Biltz and J. A. Clinch, see ref. 2. [b] Previously prepared, see ref. 3. [c] 2-Furyl. [d] For general methods of preparation and literature references to these compounds see C. R. Hauser, F. W. Swamer and J. T. Adams, in Adams, "Organic Reactions," Vol. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 59–196. [e] A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, THIS JOURNAL, 69, 1819 (1947). [f] J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1954). [g] See Experimental. [h] See ref. 3. [i] F. Swartz, *Bull. soc. acad. roy. Belg.*, [5] 12, 679 (1926).

through oxygen, nitrogen or sulfur atoms. Eventually a considerable knowledge of the chemistry of such organic compounds of uranium was evolved, and some relatively stable and volatile products were discovered.

One of the most obvious approaches to finding volatile compounds appeared to be through preparation of chelate complexes with 1,3-dicarbonyl reagents. Indeed, the uranyl and uranium(IV) acetylacetonates already had been reported.[2] We undertook the synthesis of a variety of uranium chelate compounds with 1,3-diketones and β-ketoesters, and this paper is an account of that phase of the work. At the time of our investigation, other laboratories were engaged with the same problem; consequently there was some duplication of effort. The group under Dr. H. I. Schlesinger[3] at the University of Chicago prepared a number of the same uranium compounds that we did. Many of the dicarbonyl intermediates, particularly those containing the trifluoromethyl group were synthesized for the first time during this work. Recently, some of these have been described by others.

In Table I are recorded the uranium(IV) chelates together with their melting and boiling points. These compounds ranged in color from olive-green to dark brown. They were insoluble in water but generally completely soluble in organic solvents including petroleum ether. Most of the products were purified by distilling 10 to 50-gram quantities of them in a regular claisen-type flask at greatly reduced pressure. The boiling points were fairly reproducible and gave an indication of the relative volatilities of the compounds. In order to get some idea of thermal stability, several representative compounds of Table I were placed in sealed glass tubes and heated in an oil-bath at 140° for five weeks. The uranium(IV) compounds of propionyltrifluoroacetylmethane, caproyltrifluoroacetylmethane, propionylacetone and butyrylacetone were completely decomposed. Those of dibutyrylmethane and ethyl trifluoroacetoacetate were extensively decomposed, but by fractional distillation 15 and 50%, respectively, of these compounds were recovered. All of the compounds of Table I were more or less easily oxidized. When samples were exposed to the air at room temperature they were converted within two or three weeks to what appeared to be the uranyl diketonates. Aqueous acid or base decomposed the uranium(IV) diketonates.

Three generalities can be drawn from the data of Table I: (1) The higher molecular weight compounds have lower melting points but higher boiling points. (2) Branching of carbon chains increases melting points. (3) Compounds containing trifluoromethyl in place of methyl groups are more

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(2) W. Biltz and J. A. Clinch, *Z. anorg. Chem.*, **40**, 221 (1904).

(3) H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer and R. A. Lad, THIS JOURNAL, **75**, 2446 (1953).

volatile. A considerable effort was spent in the preparation of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and the corresponding uranium(IV) chelate compound. The latter was the most volatile uranium diketonate prepared and also the least stable. It underwent some decomposition during distillation even when the bath temperature was no higher than 100°. In the air it was quite rapidly oxidized to a mixture of higher melting materials. The brown crystals were insoluble in cold dilute hydrochloric acid, but dissolved when the mixture was heated giving a green (UCl_4) solution. When the mixture was cooled and shaken, brown crystals of $U(CF_3COCHCOCF_3)_4$ were formed again.

In Table II are presented a number of uranyl diketonates. These were yellow solids. Some contained solvent of crystallization, others did not. When attempts were made to distil any of these compounds under greatly reduced pressure they decomposed completely.

TABLE II

URANYL DICARBONYL COMPOUNDS[a]

$UO_2(RCOCHCOR')_2 \cdot X$

R	R′	Solvent of crystn., X	Yield, %	M.p., °C.	Uranium, % Calcd.	Uranium, % Found
CH_3	CH_3[b,c]	H_2O	77		49.0	49.2
CH_3	C_2H_5[c]		91	218–219	48.0	48.5
CH_3	C_3H_7		90	85–86	45.5	45.2
CH_3	C_5H_{11}			95–96	41.1	40.6
CH_3	C_6H_{13}			76–78	39.1	38.9
CH_3	C_4H_3O[c,d]	C_2H_5OH	44	75–76	38.6	38.9
CH_3	C_6H_5[c]	C_2H_5OH	88	120 dec.	37.3	37.3
CH_3	o-$C_6H_4OCH_3$	$^1/_2C_2H_5OH$	92	171–172	35.3	35.3
CH_3	CF_3[c]	$^1/_2C_2H_5OH$	72	205 dec.	39.9	40.1
C_2H_5	C_2H_5	C_2H_5OH		83–84	43.4	43.8
C_3H_7	H			122 dec.	48.0	48.2
C_3H_7	C_3H_7		95	71–72	41.2	41.2
C_6H_5	C_6H_5	$^1/_2C_2H_5OH$	95	>230	32.3	32.1
CF_3	OC_2H_5	H_2O	52	125–127	36.4	36.4

[a] For references to the dicarbonyl reagents, see footnote *d*, Table I. [b] Previously prepared, see ref. 2. [c] Previously prepared, see ref. 3. [d] Furyl.

Although most of the compounds of Table I were distillable they were relatively unstable when heated, and they had rather high molecular weights. During the course of this work other more stable and more volatile compounds, particularly the uranium(V) and uranium(VI) alkoxides, were prepared. For these reasons work with the 1,3-dicarbonyl compounds was discontinued.

Experimental

Preparation of Uranium(IV) 1,3-Dicarbonyl Complexes.—The following general procedure was used for the preparation of the compounds of Table I.

To 9.5 g. (0.025 mole) of uranium(IV) chloride and 40 ml. of distilled water, a dark green solution, was added in one portion 0.10 mole of the β-diketone or β-ketoester. The mixture was warmed on the water-bath to 40° and rapidly stirred while a solution of 5.25 g. (0.05 mole) of sodium carbonate in 40 ml. of water was added dropwise. After all the sodium carbonate solution had been added the mixture was stirred at room temperature for one hour.

The compounds that separated from the reaction mixture as solids or as water-insoluble liquids were dissolved in ether, dried therein by sodium sulfate, and isolated by evaporation of ether. Purification was effected by distillation, except as noted in Table I.

Preparation of Uranyl 1,3-Dicarbonyl Complexes.—The following two examples are illustrative of the methods used to prepare the compounds of Table II.

(1) To 4.1 g. (0.027 mole) of 1,1,1-trifluoro-2,4-pentanedione and 50 ml. of water was added a solution of 6.7 g. (0.013 mole) of uranyl nitrate hexahydrate in 25 ml. of water. With shaking, a solution of 1.4 g. (0.025 mole) of potassium hydroxide in 25 ml. of water was added slowly. A bright yellow crystalline precipitate was formed, and this was collected on a filter, washed with water and air-dried. For analysis a sample was dissolved in a little ethanol and the solution was diluted with a large volume of petroleum ether (b.p. 28–38°) to precipitate the compound as yellow crystals.

(2) To a solution of 2.25 g. (0.01 mole) of dibenzoylmethane in 10 ml. of acetone was added a solution of 2.5 g. (0.005 mole) of uranyl nitrate hexahydrate in 10 ml. of water followed by a solution of 0.56 g. (0.01 mole) of potassium hydroxide in 5 ml. of water. The resulting orange, crystalline compound was collected on a filter, washed with water and recrystallized from ethanol.

Analysis.—For uranium analysis weighed samples of the compounds were digested with nitric and sulfuric acids. The digests were finally evaporated almost to dryness, the residues taken up in water, and the uranium determined with 8-hydroxyquinoline.

1,3-Dicarbonyl Coupounds.—The β-diketones and ketoesters used in the studies reported here were prepared by standard procedures.[4] Literature references are given in the footnotes of Tables I and II.

1,1,1,5,5,5-Hexafluoro-2,4-pentanedione.—This compound has been described briefly by others.[5] More details of its preparation and properties are reported here.

A solution of 1.20 moles of ethyl trifluoroacetate with 1.20 moles of sodium ethoxide in 500 ml. of anhydrous ether was allowed to react with 1.00 mole of trifluoroacetone.[5] After evaporation of the ether and heating the residue under reduced pressure, the solid was taken up in 300 ml. of ether. This solution was poured with stirring into 600 ml. of ice and water containing 34 ml. of concentrated sulfuric acid. The ether layer was separated and the aqueous layer was extracted with two 100-ml. portions of ether. The combined ether solution, separated as cleanly as possible from the water phase, was not dried but was distilled through a column until the volume had been reduced to 250 ml. The remaining liquid was cooled in an ice-bath and a mass of white, crystalline precipitate separated. The crystalline product was 1,1,1,5,5,5-hexafluoro-2,4-pentanedione dihydrate. It was collected by filtration and allowed to dry for a short time in the air. The filtrate was placed in an open dish and allowed to evaporate whereupon more of the dihydrate was obtained. The total yield was 177 g. (73%). The compound melted about 90° and decomposed. It was highly soluble in ether and somewhat soluble in water. The aqueous solution liberated carbon dioxide from sodium carbonate.

Anal. Calcd. for $C_5H_2F_6O_2 \cdot 2H_2O$: C, 24.60; H, 2.48. Found: C, 25.16; H, 2.45.

A mixture of 10 g. of the dihydrate and 30 g. of powdered, anhydrous calcium sulfate (Drierite) was heated. The colorless distillate was collected and again treated with calcium sulfate and distilled. The resulting 1,1,1,5,5,5-hexafluoro-2,4-pentanedione boiled at 68° (736 mm.), d^{25}_{25} 1.473. When the liquid was mixed with an equal volume of water and shaken it remained immiscible, but when one drop of dilute sodium hydroxide solution was added heat was produced, the diketone dissolved and, upon cooling, crystals of the dihydrate separated. The dihydrate reacted only slowly with copper acetate solution, and heating was required to produce a crystalline copper salt. The liquid, anhydrous diketone, however, reacted instantly with copper acetate solution to give a light green precipitate that turned blue-green and finally bright blue when dried. It did not melt but sublimed completely when heated in an open capillary tube.

Anal. Calcd. for $C_{10}H_2CuF_{12}O_4$: Cu, 13.31. Found: Cu, 13.03.

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(4) See refence in footnote *d*, Table I.

(5) See reference in footnote *e*, Table I.