the pyrolysis of 2-(2-chloroethoxy)-ethyl acetate. Since the latter is a new compound, its preparation and pyrolysis are described. Diglycol chlorohydrin was acetylated with acetic anhydride, and the product (94% yield) was purified by distillation: b. p. 80° (1 mm.); d^{20}_4 1.1546; $n^{20}\text{D}$ 1.4398. Found: $M^{20}\text{D}$ 38.02; C, 43.3; H, 6.8. Calcd.: $M^{20}\text{D}$ 38.07; C, 43.3; H, 6.7. Pyrolysis over Pyrex glass at 500 and 550° (contact time, 8 sec.) decomposed 32 and 83%, respectively, of the ester but produced little if any chloroethyl vinyl ether. Most of the products were gases.

PHILADELPHIA 18, PA. RECEIVED MARCH 11, 1949

Alkoxy-s-triazines. III

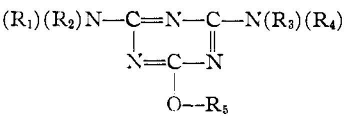
BY WILLIAM M. PEARLMAN, JACQUELINE DOWNS MITULSKI AND C. K. BANKS

In the search for antihistaminic compounds of the triazinyl ether type the alkyl 2,4-diamino-6-s-triazinyl ethers were found to have a peak of activity at the *n*-propyl compound.[1] A subsequent investigation of the methyl and butyl ethers of thirty substituted-aminotriazines disclosed no regular progression of activity as was noted in the first series.[2] Subsequently, an examination of the previously determined antihistaminic activities indicated that certain miscellaneous alkyl ethers should be prepared to determine if any products of appreciable activity had been overlooked. The ethers were prepared by previously described methods[1,2] from 2-chlorotriazines already described.[3]

The compounds were tested by Dr. Graham Chen and Mr. Charles Ensor of our laboratories by the histamine-aerosol technique of Dr. E. R. Loew.[2] The physical properties and effective antihistaminic values are recorded in the accompanying table.

TABLE I

ALKOXY-s-TRIAZINES



$(R_1)(R_2)N—C{=}N—C—N(R_3)(R_4)$; $N{=}C—N$; $O—R_5$

R_1, R_2	R_3, R_4	R_5	M. p., °C.	Yield, %	Recrystallization solvent[a]	Analyses,[b] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	A. H.[c] value (effective dose, mg./kg.)
H_2	H_2	C_5H_{11}[d]	181–183	30	Ch	48.7	48.7	7.7	7.4	25
H_2	H_2	C_5H_{11}[e]	170–172	30	B	48.7	48.7	7.7	7.3	50
H_2	H, CH_3	C_2H_5	170–171	79	H_2O-E	42.6	42.8	6.6	6.7	12.5
H_2	H, CH_3	*n*-C_3H_7	175–177	68	H_2O-P	45.9	46.1	7.2	7.2	12.5
H_2	H, CH_3	*n*-C_6H_{13}	166–168	75	H_2O-E	53.3	53.7	8.5	8.5	>50
H_2	H, CH_3	*c*-C_6H_{11}	232–234	64	H_2O-MC	54.0	54.2	7.7	7.5	12.5
H_2	H, CH_3	Phenyl	211–213	64	H_2O-D	55.3	55.5	5.1	4.9	>25
H, CH_3	H, CH_3	C_2H_5	171–173	61	H_2O-E	45.9	46.1	7.2	7.3	12.5
H_2	$(CH_3)_2$	C_2H_5	156–158	88	B	45.9	46.2	7.2	7.2	25
H, CH_3	$(CH_3)_2$	C_2H_5	173–175	80[f]	B	48.7	48.6	7.7	7.6	25
H, CH_3	$(CH_3)_2$	*c*-C_6H_{11}	154	75[f]	M	57.3	57.6	8.4	8.4	>25
H_2	H, C_5H_{11}	C_2H_5	103–105	55	H_2O-E	53.3	53.4	8.5	8.2	>25
H_2	H, C_5H_{11}	*n*-C_3H_7	92–95	46	H_2O-E	55.2	54.8	8.9	8.7	..
H, C_2H_5	H, C_2H_5	C_2H_5	116–118	44	H_2O-E	51.2	51.2	8.1	8.2	>25
H, C_2H_5	H, C_2H_5	*n*-C_3H_7	82–84	88	H_2O-E	53.3	53.5	8.5	8.4	..
H_2	C_2H_5O,[g] C_6H_5	C_2H_5	194–196 d.	83	H_2O-EC	56.7	56.7	6.2	6.1	50

[a] All compounds were colorless: B = benzene, Ch = chloroform, D = dioxane, E = ethanol, EC = Ethyl Cellosolve, M = methanol, MC = Methyl Cellosolve, P = propanol. [b] Analyses by our Microanalytical Department under the direction of Messrs. A. W. Spang and C. E. Childs. [c] See ref. 2. [d] 3-Methylbutyl. [e] 2-Methylbutyl. [f] Prepared by Mr. John Controulis. [g] Hydroxyethyl.

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(1) Controulis and Banks, THIS JOURNAL, **67**, 1946 (1945).

(2) Pearlman and Banks, *ibid.*, **71**, 1128 (1949).

(3) Pearlman and Banks, *ibid.*, **70**, 3726 (1948).

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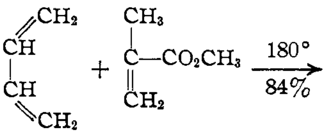
Synthesis of 3-Carbomethoxy-3-methylcyclopentanone

BY JOHN D. ROBERTS, A. K. JEYDEL AND ROSE ARMSTRONG

Ruzicka[1] has reported the preparation of 3-carbethoxy-3-methylcyclopentanone (I) through several steps from ethyl levulinate. In the present investigation, a shorter synthesis of the corresponding methyl ester (II) was achieved from the adduct of butadiene with methyl methacrylate by the following route.



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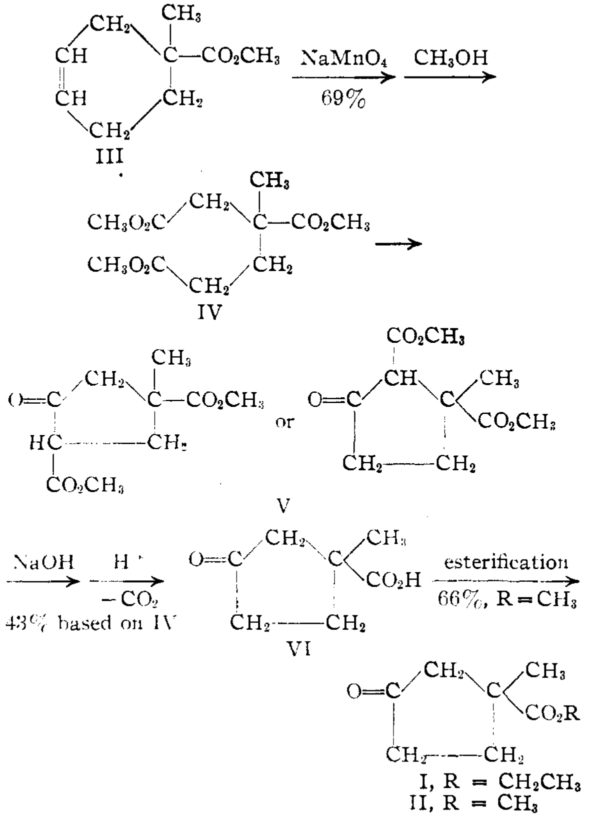
(1) Ruzicka, *Ber.*, **50**, 1362 (1917).



Experimental

4-Carbomethoxy-4-methylcyclohexene (III).—A mixture of 100 g. (1.0 mole) of methyl methacrylate, 108 g. (2 moles) of butadiene and 1 g. of hydroquinone[2] was heated in a steel hydrogenation bomb at 180° for fifteen hours. The viscous product was distilled from a Claisen flask under reduced pressure to separate the polymeric materials and the distillate fractionated through a 2 × 40 cm. glass-helix packed column. The yield of III, b. p. 64–65° (10 mm.), $n^{20}D$ 1.4600, was 130 g. (84%).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.34; H, 9.28.

In other runs at 180° for five and six hours, the yields were 64 and 71%, respectively.

Hydrolysis of III with potassium hydroxide gave **4-carboxy-4-methylcyclohexene**, m. p. 78–79° after crystallization from ligroin.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.56; H, 8.63.

Dimethyl 3-Methyl-3-carbomethoxyadipate (IV).—A mixture of 145 g. (0.94 mole) of III and 2600 ml. of water was placed in a 12-l. flask equipped with a stirrer, dropping funnel and a thermometer extending close to the bottom of the flask. The contents of the flask were stirred vigorously and a solution of 457 g. (2.3 moles) of sodium permanganate trihydrate in 2600 ml. of water added during four hours. During the addition the reaction mixture was kept saturated with carbon dioxide by adding lumps of Dry Ice every few minutes. The temperature was kept below 50° by external cooling with an ice-bath. The manganese dioxide was reduced by passing in sulfur dioxide, the solution was filtered and extracted with ether in a large continuous extractor for five days. The ether was distilled from the extract and the residue was dried by distillation with benzene using a water separator. The viscous acid remaining after distillation of the benzene was refluxed for three days with 600 g. of methanol containing 2% of dry hydrogen chloride. The excess methanol was distilled, the residue dissolved in ether, and washed with water and sodium carbonate solution. The ethereal solution was dried over magnesium sulfate and distilled through a 30-cm. Vigreux column. The yield of IV was 145 g., b. p. 120–121° (0.7 mm.), $n^{25}D$ 1.4443. An additional 9 g. of IV was obtained by esterification of the tribasic acid recovered by acidification and extraction of the sodium carbonate washings of the crude ester. The total yield was 154 g. (70%).

Anal. Calcd. for $C_9H_{18}O_6$: C, 53.65; H, 7.37; sapon. equiv., 82.1. Found: C, 53.87; H, 7.26; sapon. equiv., 83.7.

3,5(or 2,3)-Dicarbomethoxy-3-methylcyclopentanone (V).—The following procedure gave better results than the one used by Ruzicka.[1] In a three-necked creased flask equipped with a stirrer, reflux condenser and dropping funnel was placed 100 ml. of dry toluene, 100 ml. of dry xylene and 3.6 g. (0.15 mole) of clean sodium. The flask was flushed with nitrogen, the contents heated to refluxing and 64 g. (2.0 moles) of methanol added dropwise. After all of the sodium had reacted, 50 ml. of the solvent was distilled to remove most of the excess methanol. To the hot reaction mixture was added 24.6 (0.1 mole) of IV over a forty-five-minute period. The mixture was heated under reflux for two hours, then cooled and 10 ml. of acetic acid added. The mixture was treated with 150 ml. of 1 *N* hydrochloric acid and the organic layer separated, washed with water, sodium carbonate solution and dried over magnesium sulfate. After distillation of the solvent under reduced pressure the residue was fractionated through a short Vigreux column. The yield of V (which may be a mixture of isomers) was 14.6 g. (68%); b. p. 145–151° (7 mm.); $n^{25}D$ 1.4628.

Anal. Calcd. for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 56.35; H, 6.83.

3-Carboxy-3-methylcyclopentanone (VI) and 3-Carbomethoxy-3-methylcyclopentanone.—The over-all yield of VI, b. p. 140–145° (2 mm.), from IV by the previously reported procedure[1] was 43%. Esterification of VI with methyl iodide instead of ethyl iodide[1] gave 66% of II; b. p. 96° (7.5 mm.), $n^{25}D$ 1.4523.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.34; H, 8.03.

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[2] Much lower yields (20–55%) were obtained if no hydroquinone was used; *cf.* Shortridge, Craig, Greenlee, Derfer and Boord, THIS JOURNAL, **70**, 946 (1948), for similar observations.

The Catalytic Reduction of Dinitroneopentane[1]

BY JACK ROCKETT AND FRANK C. WHITMORE

The reduction of primary aliphatic nitro compounds has been found to yield, other than the primary amines, substances which are presumably reduction intermediates. These are the oxime,[2] the aldimine,[3] the nitrile,[3] and the N-hydroxylamine[4] corresponding to the nitro compound.

Among the products resulting from the hydrogenation of dinitroneopentane with Raney nickel catalyst, we have found the expected diaminoneopentane (67%) and, also, the diamide of dimethylmalonic acid (5%). The latter type substance has

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[1] This work was completed by J. R. after the untimely death of Dean Frank C. Whitmore. Thanks are due to Dr. Thomas S. Oakwood who served as adviser after the death of Dean Whitmore.

[2] Johnson and Degering, THIS JOURNAL, **61**, 3194 (1939).

[3] Kohler and Drake, *ibid.*, **45**, 1286 (1923).

[4] Hoffman and Meyer, *Ber.*, **24**, 3528 (1891).