NEW METHOD FOR THE SYNTHESIS OF MACROCYCLIC COMPOUNDS

XIV.* INTRAMOLECULAR ACYLATION OF ACID CHLORIDES OF ω-[3-(OR 4)METHYL-2-THIENYL]ALKANOIC ACIDS. SYNTHESIS OF MUSCONE

S. Z. Taits, O. A. Kalinovskii,
V. S. Bogdanov, and Ya. L. Gol'dfarb

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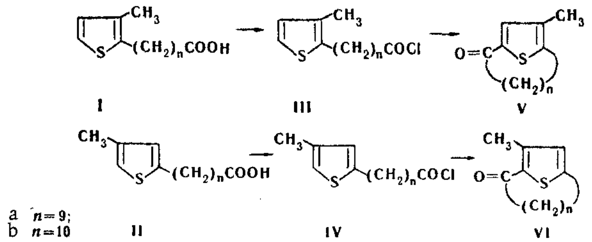
The intramolecular acylation of acid chlorides of ω-(3-methyl-2-thienyl)- and ω-(4-methyl-2-thienyl)alkanoic acids proceeds at the free 5 position of the thiophene ring. A solid-phase effect (silica gel), which, under comparable conditions, leads to more than double the yields, is displayed during the cyclization of acid chlorides of the above acids. A modification was developed for the reductive desulfurization of cyclothienones with alkyl groups in the β position of the thiophene ring; the modification includes the formation of unsaturated compounds and products of the reduction of the carbonyl group. A new route to the synthesis of γ- and β-methylcycloalkanones, including DL-muscone, was developed.

We described the intramolecular acylation of acid chlorides of ω-(α-methylthienyl)alkanoic acids as a method for the synthesis of α-alkyl-substituted macrocyclic ketones in previous communications [1, 2]. It seemed of interest to study the possibility of the use of β-methylthiophene to obtain the corresponding thienylalkanoic acids, from which one might be able to arrive at β- and γ-alkyl-substituted macrocyclic ketones, particularly muscone, which is one of the most valuable natural aromatic compounds that have the odor of musk. In this paper, we present the results of an investigation of routes to the synthesis of ω-(β-methylthienyl)alkanoic acids and the conditions for the cyclization of their acid chlorides:



The reductive desulfurization of the cyclothienones to the corresponding alkyl-substituted cycloalkanones was also investigated.

Thienylalkanoic acids of the I and II type can be obtained from 3-methylthiophene via schemes previously used for unsubstituted thiophenes [3, 4]:

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*See [2] for communication XIII.

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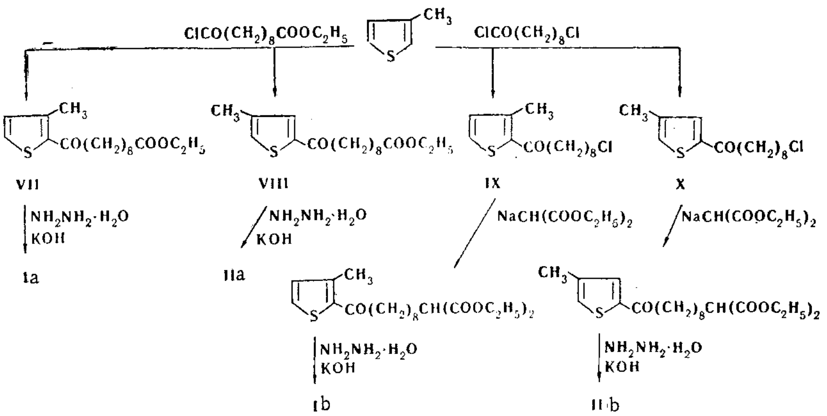
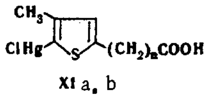


As should have been expected, judging from the data available in the literature [5, 6], mixtures of 2- and 5-substituted 3-methylthiophenes are formed in the acylation of 3-methylthiophene. According to the results of gas-liquid chromatography (GLC), in our case these isomers were formed in a ratio of 2 : 1. In addition, a slight amount of the corresponding ketone containing a CH_3 group in the 2 position of the thiophene ring is always present in the mixture of ketones obtained. This ketone is formed from the 2-methylthiophene always present in 3-methylthiophene, both in the product synthesized from 3-formylthiophene by Kishner reduction and in the products synthesized catalytically from isoprene and hydrogen sulfide. The amount of it in various samples may vary over rather a broad range. In our case, the starting 3-methylthiophene contained 3.4-3.8% 2-methylthiophene.*

The ketones were separated without substantial losses by partition chromatography into two fractions, one of which is pure ketone VII (or IX), according to PMR spectroscopy. An AB type of spectrum† is observed at weak field for VII with $\delta_A = 7.30$ and $\delta_B = 6.86$ ppm, $J_{A,B} = 4.8$ Hz, $J_{CH_3,4\text{-}H} = 0.4$ Hz, and $J_{CH_3,5\text{-}H} = 0.3$ Hz. The very character of the spectrum and the magnitude of the spin–spin coupling constant are evidence for the adjacent orientation of the protons attached to the double bond [7], which is in agreement with the structure that we ascribed to VII. A similar PMR spectrum is observed for IX ($\delta_A = 7.28$ ppm, $\delta_B = 6.85$ ppm, $J_{A,B} = 4.9$ Hz, $J_{CH_3,4\text{-}H} = 0.4$ Hz, $J_{CH_3,5\text{-}H} = 0.3$ Hz). In addition to the fundamental signals of the protons of the thiophene ring,‡ which correspond to the proposed structure ($\delta_A = 7.42$ ppm and $\delta_B = 7.13$ ppm, $J_{H_A,CH_3} = 1.4$ Hz, and $J_{H_B,CH_3} = 0.9$ Hz), a signal at $\delta = 6.72$ ppm, which is the strong-field portion of the AB spectrum of 5-methyl-2-thienyl 8-carbethoxyoctyl ketone, is observed in the second chromatographic fraction (ketones VIII or X). These fractions are consequently mixtures of ketones VIII or X with the corresponding ketones that are derivatives of 2-methylthiophene. This assumption is confirmed by recording the spectrum of pure 5-methyl-2-thienyl 8-carbethoxyoctyl ketone. Pure acids Ia and Ib (according to PMR spectroscopy) were obtained by Kishner reduction of ketone VII and, in the other case, by the reaction of ketone IX with malonic ester and subsequent reduction. As a result of subsequent transformations (reduction or reaction with malonic ester and Kishner reduction with simultaneous saponification and decarboxylation without purification), ketones VIII and X gave a mixture of IIa and 10-(5-methyl-2-thienyl)capric acid or a mixture of IIb and 11-(5-methyl-2-thienyl)undecanoic acid. Pure acids IIa and IIb were isolated by treatment of solutions of these mixtures with alcoholic mercuric chloride. It is known [8] that thiophene derivatives with a free α position in the ring are readily mercurated, while thiophene derivatives in which the α positions are substituted can be mercurated only with mercuric acetate. In the reaction of IIa and IIb with mercuric chloride, their mercury derivatives (XI) precipitate practically quantitatively, while the acids that are 2-methylthiophene derivatives remain in solution. The chloromercuri derivatives (XIa, b) were converted by known methods [9] to IIa and IIb, which do not contain impurities, according to PMR spectroscopy.



XI a, b

a $n=9$; b $n=10$

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*Determined by means of GLC with a 5-m long column filled with 5% polyethylene glycol 2000 on Chromosorb W at 122°C.

†The symbols H_A and H_B are the protons in the 5 and 4 positions of the thiophene ring, respectively.

‡The symbols H_A and H_B are the protons in the 5 and 3 positions of the thiophene ring, respectively.

TABLE 1. α-Cyclothienones

Compound	Amt. of starting acid, g	Mp., °C	Empirical formula	Found				Calc.				Yield, %^{a}	
				C, %	H, %	S, %	M^b	C, %	H, %	S, %	M	with silica gel	without silica gel
12-Methyl-[10]-α-cyclothienone	5	58,5—60^d	$C_{15}H_{22}OS$	71,7	8,7	12,9	254	71,9	8,9	12,8	250	55	27
13-Methyl-[10]-α-cyclothienone	5	90—91,5^e	$C_{15}H_{22}OS$	72,1	9,0	12,7	246	71,9	8,9	12,8	250	57	26
13-Methyl-[11]-α-cyclothienone	5	40,5—42^g	$C_{16}H_{24}OS$	72,6	9,2	12,1	258	72,7	9,2	12,1	264	72	55
14-Methyl-[11]-α-cyclothienone	1	76,5—78,5^e	$C_{16}H_{24}OS$	72,7	9,3	12,1	258	72,7	9,2	12,1	264	33^h	14

a) The yields of the ketones were determined by both GLC (215°, He as the gas carrier at 40 ml/min, a 1-m long column filled with 5% 1,4-butanediol succinate on Chromosorb G (60/80 mesh); thienocyclohexanone was used as the internal standard) and by direct isolation of the ketone. The values obtained were in agreement with an accuracy of up to 3%.

b) Ebullioscopically in benzene.

c) The p-nitrophenylhydrazone had mp 128-131° (dec.) and was a mixture of syn and anti isomers. Found: N 10.9%. $C_{21}H_{27}N_3O_2S$. Calculated: N 10.9%.

d) From hexane.

d) From heptane.

f) The p-nitrophenylhydrazone was the yellow isomer with mp 145-148° (dec.). Found: C 66.3; H 7.2; S 7.9%. $C_{22}H_{29}N_3O_2S$. Calculated: C 66.1; H 7.3; S 8.0%.

g) The red isomer with mp 125° (dec.). Found: C 66.5; H 7.4; S 8.2%.

h) When the experiment was carried out with a larger amount of the starting acid chloride (3.8 g), the yield in a heterogeneous medium reached 56%.

TABLE 2. Methylcycloalkanones

Compound	Mp, °C	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calc., %		Semicarbazone		
				found	calc.		C	H	C	H	mp, °C	N, % found	N, % calc.
γ-Methylcyclotetradecanone	28,5—29,5^{a,b}	—	—	—	—	$C_{15}H_{28}O$	79,9	12,2	80,3	12,6	170—172^{a,c}	15,3	14,9
β-Methylcyclotetradecanone	31,5—33,5^{b,d}	—	—	—	—	$C_{15}H_{28}O$	80,3	12,6	80,3	12,6	135—137^{b,d}	15,3	14,9
γ-Methylcyclopentadecanone	—	0,9187	1,4792	73,61	73,35	$C_{16}H_{30}O$	80,2	12,8	80,6	12,7	150—152^{c,e}	14,5	14,2
β-Methylcyclopentadecanone DL-muscone	—	0,9177^f	1,4782	73,56	73,35	$C_{16}H_{30}O$	80,8	12,8	80,6	12,7	132—134^{b,d}	14,3	14,2

a) Literature data: mp 28-29°; the semicarbazone had mp 182-183° [13].

b) From hexane.

c) From alcohol.

d) Literature data: mp 28-29°, semicarbazone mp 140-141.5° [14].

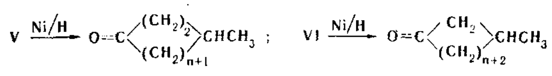
e) Literature data: mp 161-162° [13].

f) Literature data: mp 133-133.5° [15], 133.5-134.5° [16], but there are indications of mp 138-140° [17] and 140-141° [18]. This scatter in the melting points is apparently explained by different ratios of the syn and anti forms of the semicarbazones in the preparations obtained; d_4^{20} 0.9193 [19].

The corresponding ω-(5-methyl-2-thienyl)alkanoic acids were isolated from the mother liquors and identified. Acid chlorides III were obtained by the usual method [1, 2]; they are about as stable as the acid chlorides of ω-thienylalkanoic acids that we previously used in intramolecular acylation reactions, whereas acid chlorides IV proved to be considerably more labile compounds. In the preparation of IV by the usual method – the action of thionyl chloride in ether solution on acids II – they were almost completely resinified in a period of time that was considerably less than required for completion of the cyclization. This instability of acid chlorides IV is apparently explained by the increased reactivity of the 5 position, which is activated by both the heteroatom and the methyl group in the ortho position. Intermolecular acylation, which, in this case, leads to resinification, apparently occurs under the influence of the weak catalytic action of the HCl evolved during the action of thionyl chloride on acid II. In fact, completely stable solutions of acid chlorides IV that did not change over a considerable period of time were obtained in ether or hexane in the presence of pyridine (which ties up the HCl). The reaction in both homogeneous media and in the presence of silica gel was studied during the selection of the conditions for the cyclization of acid chlorides III and IV. In [1], it was noted that, in the case of the acid chlorides of ω-(5-methyl-2-thienyl)alkanoic acids, the presence of silica gel in the reaction mixture leads to certain complications during intramolecular acylation, and this compelled us to use the process in a homogeneous medium with an increased concentration of $AlCl_3$-etherate. The yields of the product of intramolecular acylation in the presence of silica gel in the cyclization of acid chlorides III and IV is about twice the yield of product in homogenous media under completely comparable conditions (for example, see [3]). According to the results of elementary analysis and the molecular weights, the cyclothienones obtained (Table 1) correspond to the structures presented.

The signal of the ring proton in the PMR spectrum of cyclothienone V has a chemical shift of 7.02 ppm, while the chemical shift of the ring proton in cyclothienone VI is 6.55 ppm. The shift in the signal of the ring proton in cyclothienone V to weak field attests to its deshielding by the carbonyl function, indicating that they are attached to adjacent ring carbon atoms.

Data on the reductive desulfurization of the cyclothienones obtained constitute a confirmation of their structure; known alkyl-substituted cycloalkanones are formed in this case. Cyclothienones V give γ-methylcycloalkanones, while VI give β-methylcycloalkanones (in particular, VIb gives muscone):

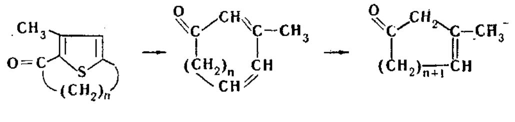


$$V \xrightarrow{Ni/H} O{=}C\left\langle\begin{matrix}(CH_2)_2\\(CH_2)_{n+1}\end{matrix}\right\rangle CHCH_3\ ; \quad VI \xrightarrow{Ni/H} O{=}C\left\langle\begin{matrix}CH_2\\(CH_2)_{n+2}\end{matrix}\right\rangle CHCH_3$$

a $n=9$; b $n=10$

It should be noted that the reductive desulfurization of the cyclothienones described in this paper, which have a methyl group in the β position of the thiophene ring, proceeds with greater difficulty than in the case of unsubstituted cyclothienones or cyclothienones with alkyl groups in the α position. The cleavage of sulfur is completed quite rapidly when the compounds are treated with the usual amount of Raney nickel, but full hydrogenation is not complete even after 4 h, and the reaction product contains up to 20% of the β,γ-unsaturated ketone, according to UV spectroscopy. The addition of additional amounts of Raney nickel does not substantially accelerate the process and leads to the reduction of the carbonyl function, since the inhibiting action of acetone is overcome when large excesses of Raney nickel are present [10]. The reduction of the carbonyl function is readily followed from the IR spectrum of the reaction product: an absorption band appears in it at 3387 cm^{-1}, which corresponds to the alcohol hydroxyl group. From the above, we modified the usual method for the reductive desulfurization by treating the cyclothienone in alcohol–acetone solution with the minimum amount of Raney nickel sufficient to tie up the sulfur; after removal of the nickel, the reaction product was hydrogenated in alcohol at normal pressure in the presence of Pd on carbon. The hydrogenation products were isolated in the usual way, except that when traces of the secondary alcohol were observed in them, it was separated by chromatography. The ketones obtained and their yields and physical constants are presented in Table 2.

The examined difference in behavior with respect to Raney nickel of the β-methylcyclothienones can be explained by the peculiarities of their structures. It is known that the first act in the reaction of thiophene derivatives with Raney nickel [11, 12] is cleavage of the C–S bond:



The diene formed can react with hydrogen via both a 1,2-addition scheme and a 1,4-addition scheme; in the latter case, an unsaturated compound with a shielded "trisubstituted" double bond, which is extremely difficult to hydrogenate over Raney nickel catalysts (see [20, 21], for example), will be formed.

EXPERIMENTAL

The PMR spectra were recorded with a DA-60IL spectrometer. Gas-liquid chromatography was carried out with an LKhM-7a chromatograph (Mosneftekip Plant). The molecular weights were determined with an ÉP-2 ebulliograph from the Special Design Office, N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR.

3-Methyl-2-thienyl and 4-Methyl-2-thienyl 8-Carbethoxyoctyl Ketones (VII and VIII). A total of 14.9 g (94%) of a mixture of ketones with bp 177-180° (0.05 mm) was obtained under the conditions in [1] from 5 g (0.05 mole) of 3-methylthiophene and 13.2 g (0.053 mole) of the acid chloride of the monoethyl ester of sebacic acid in the presence of 13.2 g (0.05 mole) of $SnCl_4$. A 110 g sample of this mixture was separated by chromatography on 700 g of activity III Al_2O_3 with a 25-cm long column and 5% ether in hexane as the eluent. After routine separation, the column was washed thoroughly with ether and hexane, and a new portion of the substance was introduced on the same sorbent. Losses up to 14% were initially observed due to irreversible adsorption of the substance on aluminum oxide; these losses were reduced to 2-3% after three successive separations on the same adsorbent. A total of 62 g of ketone VII and 34.7 g of ketone VIII were obtained. 3-Methyl-2-thienyl 8-carbethoxyoctyl ketone had n_D^{20} 1.5111, d_4^{20} 1.0556, and R_f 0.12 (thin-layer chromatography on Al_2O_3 in benzene was used in all cases). Found: C 65.5; H 8.4; S 10.3%; MR_D 88.12. $C_{17}H_{26}O_3S$. Calculated: C 65.8; H 8.4; S 10.3%; MR_D 87.89. Refluxing 0.5 g of this ketone in 5 ml of alcohol with 1 ml of 10% NaOH gave 9-(3-methyl-2-thenoyl)nonanoic acid with mp 68.5-70° (from hexane–toluene). Found: C 63.9; H 7.7; S 11.4%. $C_{15}H_{22}O_3S$. Calculated: C 63.8; H 7.8; S 11.4%. According to PMR spectroscopy, ketone VIII contained 12% 5-methyl-2-thienyl 8-carbethoxyoctyl ketone. Found: C 65.9; H 8.8; S 10.2%. $C_{17}H_{26}O_3S$. Calculated: C 65.8; H 8.4; S 10.3%.

3-Methyl-2-thienyl and 4-Methyl-2-thienyl 8-Chlorooctyl Ketones (IX and X). A total of 90.3 g (81%) of a mixture of ketones with bp 174-176° (0.8 mm) was obtained from 40 g (0.41 mole) of β-methylthiophene and 88 g (0.42 mole) of ω-chlorononanoyl chloride via the method in [2]. This mixture was separated by chromatography to isolate 57 g of IX and 31.5 g of a mixture of X and 5-methyl-2-thienyl 8-chlorooctyl ketone. Compound IX had n_D^{20} 1.5330, d_4^{20} 1.0960, and R_f 0.59. Found: C 61.8; H 7.3; Cl 12.9; S 11.6%; MR_D 77.38. $C_{14}H_{21}ClOS$. Calculated: C 61.6; H 7.8; Cl 13.0; S 11.7%; MR_D 77.25. Compound X contained 12% 5-methyl-2-thienyl 8-chlorooctyl ketone. Found: C 61.8; H 7.8; Cl 12.9; S 11.6%. $C_{14}H_{21}ClOS$. Calculated: C 61.6; H 7.8; Cl 13.0; S 11.7%.

10-(3-Methyl-2-thienyl)capric Acid (Ia). The Kishner reduction [1] of 30 g (0.097 mole) of ketone VII gave 20 g (78%) of a product with mp 40-42° (from hexane). Found: C 67.2; H 9.0; S 11.8%. $C_{15}H_{24}O_2S$. Calculated: C 67.1; H 9.0; S 11.9%. The anilide had mp 67-69° (from ether). Found: C 73.4; H 8.6; S 9.2%. $C_{21}H_{29}NOS$. Calculated: C 73.4; H 8.5; S 9.3%.

10-(4-Methyl-2-thienyl)capric Acid (IIa). The reduction of 10 g (0.032 mole) of a mixture of VIII and 5-methyl-2-thienyl 8-carbethoxyoctyl ketone via the method indicated above gave 7.9 g (91%) of IIa containing 10-(5-methyl-2-thienyl)capric acid. For separation, a mixture of 19.2 g (0.038 mole) of the crude substance, 650 ml (0.15 mole) of saturated $HgCl_2$ solution, 120 ml (0.45 mole) of saturated sodium acetate solution, and 1.2 liter of alcohol was shaken for 1 h, and 10-(5-chloromercuri-4-methyl-2-thienyl)capric acid (XIa) with mp 116-117.5° (from alcohol) was removed by filtration after 12 h. Found: C 36.0; H 4.7%. $C_{15}H_{23}ClHgO_2S$. Calculated: C 35.8; H 4.6%. Compound XIa was refluxed for 5 min with 6% hydrochloric acid. The mixture was cooled, and 14.7 g (75%) of pure IIa with mp 54.5-55.5° (from hexane) was removed by filtration. Found: C 67.0; H 9.0; S 12.3%. $C_{15}H_{24}O_2S$. Calculated: C 67.1; H 9.0; S 11.9%. The anilide had mp 86-88.5° (from ether). Found: N 4.0%. $C_{21}H_{29}NOS$. Calculated: N 4.1%.

11-(3-Methyl-2-thienyl)undecanoic Acid (Ib). The reaction of 20 g (0.074 mole) of 3-methyl-2-thienyl 8-chlorooctyl ketone with sodiomalonic ester (from 0.15 mole of freshly distilled malonic ester and 0.12 g-atom of sodium) and 2 g of anhydrous NaI [2] gave 12.2 g (54%) of a product with mp 47.5-49.5°. Found: C 68.0; H 9.2; S 11.4%. $C_{16}H_{26}O_2S$. Calculated: C 68.0; H 9.3; S 11.3%. The anilide had mp 62-63° (from alcohol). Found: C 73.8; H 8.8; S 8.9%. $C_{22}H_{31}NOS$. Calculated: C 73.9; H 8.7; S 9.0%.

11-(4-Methyl-2-thienyl)undecanoic Acid (IIb). The above method gave 6.2 g (73%) of a mixture of IIb and 11-(5-methyl-2-thienyl)undecanoic acid from 8.2 g (0.03 mole) of a mixture of X and 5-methyl-2-thienyl 8-chlorooctyl ketone. Compound IIb was purified through mercury derivative XIb. Pure IIb had mp 52-54° (from hexane). Found: C 67.9; H 9.2; S 11.3%. $C_{16}H_{26}O_2S$. Calculated: C 68.0; H 9.3; S 11.3%. The anilide had mp 66-67° (from heptane–toluene). Found: N 4.2%. $C_{22}H_{31}NOS$. Calculated: N 3.9%.

12-Methyl-[10]-α-cyclothienone (Va). Pyridine (1.5 ml) was added to a solution of 5 g (0.019 mole) of acid Ia in 25 ml of absolute ether, the mixture was cooled to 0°, and 5 ml of thionyl chloride was added slowly with stirring. After stirring the mixture for 1 h at 20°, the solvent and excess thionyl chloride were removed by distillation without access to air moisture and with simultaneous addition of dry heptane in such a way that the volume of the mixture was no less than 10 ml. The solution of the acid chloride in heptane was removed by filtration under dry nitrogen pressure from the precipitated pyridine hydrochloride. The filtrate was brought up to a volume of 45 ml with heptane and separated into two equal portions. The first portion was added by means of a syringe at a rate of 3.5 ml/h through a packing for high dilution [3] to a vigorously stirred and refluxing mixture of 15 g of $AlCl_3$ · etherate and 50 g of silica gel in 260 ml of chloroform. The second portion was added under similar conditions to a solution of 15 g of $AlCl_3$ · etherate in 260 ml of chloroform. The addition was complete in 6.5 h, after which the reaction mixtures were refluxed for another 2 h, cooled to below 15°, and 150 ml of dilute (1 : 10) hydrochloric acid was added gradually to them. After the usual workup [1], 1.3 g (55%) and 0.64 g (27%) of ketone Va, respectively, were obtained from the experiments with and without silica gel. The other cyclothienones were similarly synthesized (see Table 1).

β-Methylcylopentadecanone (Muscone). A solution of 2.1 g of cyclothienone VIb in 70 ml of alcohol and 50 ml of acetone was stirred with 20 g of Raney nickel at 30-35° until the mixture gave a negative reaction for sulfur (2 h). The nickel was removed by filtration and washed thoroughly with alcohol, and the wash liquid was combined with the bulk of the filtrate. This mixture was then evaporated, and the residue was dissolved in 40 ml of alcohol and hydrogenated over 2 g of 5% palladium on carbon at 20° and atmospheric pressure until hydrogen absorption ceased (4 h). The catalyst was removed by filtration and washed thoroughly with alcohol. The filtrate was vacuum evaporated, and the residue was dissolved in heptane. The heptane solution was washed with water to pH 7 and dried with $MgSO_4$. The solvent was evaporated, and the residue was sublimed at 100° (0.1 mm). The resulting product was purified by chromatography with a column filled with activity III Al_2O_3 with elution by a 5% solution of ether in benzene, and the ketone fraction was again vacuum sublimed. The other ketones were similarly obtained (see Table 2).

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