

It was found that alkaline Raney nickel gave material which could not be crystallized. Well-washed Raney nickel gave material which after recrystallization from Skellysolve F at -10° melted at $42-44^{\circ}$ (reported⁴ m.p. $41-42^{\circ}$).

cis-Phenylcyclohexyl methyl xanthate was prepared by the method of Alexander and Mudrak³ except that the lithium salt of the alcohol, prepared by means of phenyllithium in ether, was used rather than the sodium salt prepared by the action of sodium in ether. The xanthate was obtained as crystals, m.p. $47-50^{\circ}$ (reported³ m.p. $49-50^{\circ}$).

Pyrolysis of Methyl *cis*-2-Phenylcyclohexylxanthate.—The method of Alexander and Mudrak³ was used. A 300-ml. flask was equipped with an efficient spiral condenser which was vented *via* a mercury bubbler to a flask containing 45% potassium hydroxide solution which in turn was vented to a hood. In the flask was placed 20.0 g. (0.075 mole) of the xanthate and the flask heated by a metal-bath to 215° for 40 minutes and then to $235-240^{\circ}$ for five minutes. The condenser was washed with a small amount of pentane and the product distilled through a 12-cm. Vigreux column to give the following fractions: (1) 1.63 g., b.p. $84-86^{\circ}$ at 2.3 mm., n_D^{25} 1.5417, λ_{max} 260 $m\mu$ (ϵ 356), at 248 $m\mu$, ϵ 232; (2) 4.80 g., b.p. 86° at 2.3 mm., 85° at 2.2 mm., n_D^{25} 1.5418; (3) 4.95 g., b.p. 85° at 2.2 mm. (also contained material chased from the column by use of an infrared heat lamp), n_D^{25} 1.5421, λ_{max} 260 $m\mu$ (ϵ 647), at 248 $m\mu$, ϵ 605; total yield, 11.38 g., 95.5% of theory. The sample of 3-phenylcyclohexene prepared by the method of Berlande⁹ had n_D^{25} 1.5432, λ_{max} 253 $m\mu$ (ϵ 816), at 248 $m\mu$, ϵ 787. The infrared spectra of fractions 1 and 3 were identical. The spectrum of Collins' sample¹ determined at the same time was identical with the above spectra except that a few of the shoulders were of slightly higher intensity.

A sample of 1-phenylcyclohexene had n_D^{25} 1.5664; λ_{max} 248 $m\mu$ (ϵ 12,170).

Phenylcyclohexane. A. From 1-Phenylcyclohexene.—A mixture of 15.8 g. (0.10 mole) of 1-phenylcyclohexene, 25 ml. of methanol, and 100 mg. of 10% palladium-on-charcoal was shaken in a hydrogen atmosphere in a Parr apparatus. The hydrogen uptake became slow after 44 minutes (6.0 lb. used, 86% of theory) so the reaction was stopped, the catalyst removed by filtration, and the product distilled to give (1), 8.3 g., b.p. $111-113^{\circ}$ at 13 mm., n_D^{25} 1.5250; (2), 3.1 g., b.p. $113-115^{\circ}$, n_D^{25} 1.5278.

B. From 3-Phenylcyclohexene.—A mixture of 1.0 g. (6.33 mmoles) of 3-phenylcyclohexene, 150 mg. of 10% palladium-on-charcoal and 15 ml. of methanol was stirred in an atmospheric pressure hydrogenation apparatus. In 35 minutes 158 ml. (100% of theory) of hydrogen was absorbed. The catalyst was removed by filtration, the methanol solution diluted with water and extracted with pentane, and the pentane extract washed with water, filtered and distilled. There was obtained 0.90 g. (90%) of product, b.p. 59° at 0.5 mm., n_D^{25} 1.5237; reported for phenylcyclohexane,¹⁴ b.p. 238° , n_D^{25} 1.5249. The infrared spectra of the two samples showed them to be the same compound.

Behavior of 3-Phenylcyclohexene under Hofmann Conditions.—A mixture of 1.58 g. (0.01 mole) of 3-phenylcyclohexene, 0.6 g. (0.01 mole) of potassium hydroxide and 1.0 g. (0.01 mole) of triethylamine in 30 ml. of water was refluxed for 1.5 hours. The cooled mixture was then extracted with pentane and the pentane extract washed successively with water, 6 *N* hydrochloric acid, water, saturated sodium bicarbonate solution, and water again. The pentane solution was then filtered and distilled to give 1.45 g. (91.7% recovery) of material, b.p. 80° at 1.7 mm., n_D^{25} 1.5418, infrared spectra identical with the starting material. High recovery was attained in this and the subsequent experiments by forcing the last traces of material out of the distillation column by means of an infrared lamp. This was necessary in order not to lose any 1-phenylcyclohexene which boils higher than the 3-phenylcyclohexene.

The above experiment was repeated using 25 ml. of isopropyl alcohol and 10 ml. of water instead of pure water as solvent. On distillation 1.30 g. (82%) of material was recovered, b.p. 81.5° at 1.7 mm., n_D^{25} 1.4512, infrared spectrum identical with starting material.

Isomerization of 3-Phenylcyclohexene.—Fifty ml. of a solution containing 5.60 g. (0.0352 mole) of 3-phenylcyclohexene and 2.10 g. (0.0375 mole) of potassium hydroxide

in commercial absolute alcohol was prepared. Ten-ml. aliquots were placed in Pyrex tubes, flushed with nitrogen, and sealed. The tubes were placed in a 100° steam-bath and removed after the stated intervals. A small amount of a white solid separated from solution when the tubes were first heated. The phenylcyclohexene was recovered by diluting the contents of a tube with water, extracting with pentane, washing the pentane layer, and distilling. In each case about 85% of the olefin was recovered. The refractive index was determined immediately after distillation and this used to calculate the percentage of isomerization.

Time, hours	n_D^{25}	Isomerized, %
0.25	1.5418	0
24	1.5428	4.5
96	1.5442	9.8
192	1.5453	14.2

The above samples on standing in stoppered clear glass vials on a desk top for between five and fifteen days had the following n_D^{25} : 1.5445 (15 days), 1.5430 (5 days), 1.5460 (10 days), 1.5456 (5 days). Ultraviolet absorption spectra measurements on the 2 five-day specimens gave percentage compositions which checked those determined by refractive index to within 1%. Apparently 3-phenylcyclohexene is not stable toward light and air; formation of a hydroperoxide seems likely since the sample gave a strong positive test with aqueous potassium iodide in the presence of acetic acid.

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Oxidation of Methyl 8-Nitrodehydroabietate

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At the time that the chromic acid degradation of methyl 6,8-dinitrodehydroabietate was being studied² a concurrent investigation of the oxidation of methyl 8-nitrodehydroabietate (I) and methyl dehydroabietate (VIII) was being made. We wish now to record the results of this work and in particular to report the successful degradation of the isopropyl side chain of the dehydroabietic structure with chromic acid.

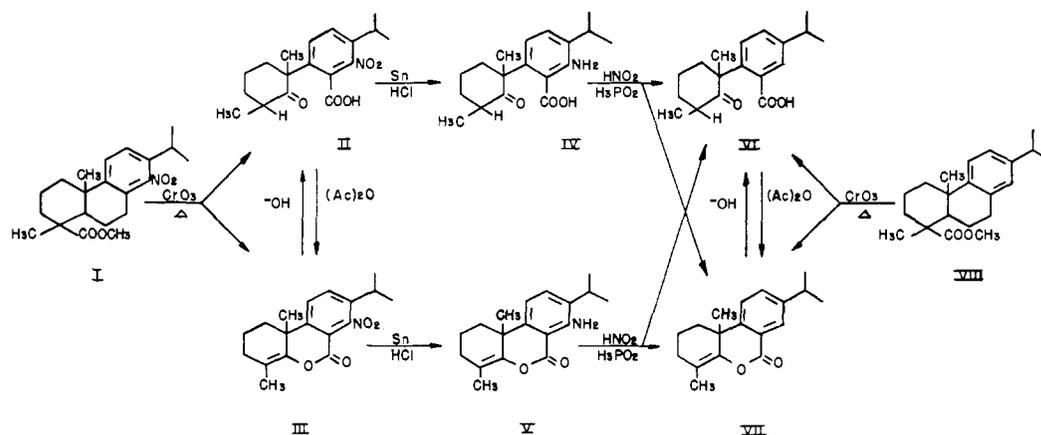
In acetic acid with chromium trioxide at 70° I gives rise to an acidic mixture which loses carbon dioxide at 160° . The decarboxylated product is separable into neutral and acidic crystalline fractions which are interconvertible by treating the former with base and the latter with acetic anhydride. On the basis of physical properties, analyses, ultraviolet and infrared spectra and analogy with the degradation products of methyl 6,8-dinitrodehydroabietate,² the neutral substance is formulated as the nitro enol lactone III and the acidic fraction as the nitro keto acid II.

Reduction of II and III with tin and hydrochloric acid gave the corresponding amino keto acid IV and amino enol lactone V. Hypophosphorous acid deamination led to the same two products, neutral and acidic, whether the substance diazotized was IV or V. Furthermore, these two products were interconvertible with the same reagents as II and III. The neutral substance, therefore, is the enol lactone VII and the acidic product the keto acid VI. Assuming that the oxidation of methyl dehydroabietate (VIII) would follow the same path as that of I, the acidic fraction arising from the oxidation of VIII should give,

(1) Monsanto Chemical Company, Dayton 7, Ohio.

(2) E. S. Hansen and H. H. Zeiss, *THIS JOURNAL*, **77**, 1643 (1955).

(14) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 265.



after decarboxylation, VI and VII. Not only did VIII give these products but also 1,12-dimethyl-1-carbomethoxy-7-acetyl-1,2,3,4,9,10,11,12-octahydro-9-phenanthrone (IX) as a neutral fraction directly from the oxidation mixture in 17–20% yield. This substance also has been obtained recently from VIII in three steps.³

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Experimental⁴

Oxidation of Methyl 8-Nitrodehydroabietate (I).—Methyl 8-nitrodehydroabietate, m.p. 192–193°, prepared according to the procedure of Campbell and Morgana⁵ with several advantageous modifications, was oxidized with chromic acid at 70° for 10 hours as described for methyl 6,8-dinitrodehydroabietate.² Two grams of an acidic fraction, m.p. 140–150°, was obtained from 3.6 g. of starting ester. A total of 3.78 g. of this crude acid was heated between 150–160° under vacuum for several minutes, during which the evolution of carbon dioxide was observed. After the foaming had subsided, 3.32 g. of a clear brittle melt remained.

(a) **Isolation of the Nitro Keto Acid II.**—An ether solution of the melt was extracted with 1 *N* sodium hydroxide solution, and this extract, upon acidification with dilute hydrochloric acid, gave 1.8 g. of a white precipitate of II which was crystallized from ethanol as brilliant prisms, m.p. 231–232°, $[\alpha]_D + 296^\circ$ (c 0.7), λ_{\max} 230 and 285 μ [$\log \epsilon$, 3.21 and 1.86].

Anal. Calcd. for C₁₅H₂₃O₅N: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.85; H, 6.88; N, 4.12.

After heating 0.1 g. of II in 10 ml. of acetic anhydride for 24 hours at 160°, the solution was cooled, treated with 50 ml. of water and reheated on the steam-bath for 20 minutes. On cooling a white precipitate formed which was collected and crystallized from ethanol: 80 mg. of the enol lactone III, m.p. 206–208°, which melted undepressed with the substance isolated just below.

Anal. Found: C, 68.77; H, 6.96; N, 4.46 (*vide infra*).

(b) **Isolation of the Nitro Enol Lactone III.**—Evaporation of the ether from the neutral fraction separated as above left 0.2 g. of a white solid which was crystallized from ethanol in the form of needles, m.p. 208–209°, $[\alpha]_D + 409^\circ$ (c 0.23), λ_{\max} 232 and 290 μ ($\log \epsilon$ 4.0 and 2.44). Its infrared spectrum showed characteristic enol lactone absorption at 5.72 and 5.87 μ .

Anal. Calcd. for C₁₅H₂₁O₄N: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.64; H, 6.81; N, 4.66.

(3) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, *THIS JOURNAL*, **76**, 723 (1954).

(4) All m.p.s. are corrected. Optical rotations (*D*-line) were measured in 95% ethanol in a 1-dm. tube at room temperature. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Ultraviolet spectra were measured in 95% ethanol and infrared spectra in chloroform.

(5) W. P. Campbell and M. Morgana, *THIS JOURNAL*, **63**, 1838 (1941).

The enol lactone (15 mg.) was refluxed with 10 ml. of 5% aqueous alcoholic (1:1) sodium hydroxide for 10 minutes. After dilution of the clear solution with 50 ml. of water, the solution was extracted with ether. Acidification of the alkaline layer gave a resinous material which was crystallized from ethanol, m.p. 229–230°. Mixed m.p. and comparison of infrared spectra were used to identify this substance as the keto acid II.

Reduction of II and III to their Corresponding Amino Compounds (IV and V).—One g. of II was dissolved in 20 ml. of acetic acid on the steam-bath. After adding 1 g. of tin powder, 5 ml. of concentrated hydrochloric acid was added dropwise to the mixture over a period of 20 hours. The decantate was diluted with water, and the resultant turbid mixture was extracted with ether. Thorough washing of the ether solution followed by evaporation of the solvent left a white solid which was crystallized from ethanol and a small amount of water as needles of the amino keto acid IV, m.p. 185–186°, $[\alpha]_D + 125^\circ$ (c 1.33).

Anal. Calcd. for C₁₅H₂₅O₅N: C, 71.25; H, 8.31; N, 4.62. Found: C, 70.66; H, 8.63; N, 4.75.

Repetition of the above experiment on 300 mg. of the nitro enol lactone III and recrystallization of the product from ethanol gave 110 mg. of the amino enol lactone V, m.p. 86–87°, $[\alpha]_D + 133.5^\circ$ (c 0.48).

Anal. Calcd. for C₁₅H₂₃O₅N: C, 75.75; H, 8.12; N, 4.91. Found: C, 76.09; H, 8.57; N, 5.18.

Deamination of IV and V to the Keto Acid VI and the Enol Lactone VII.—The amino keto acid IV, 340 mg., was diazotized in 0.5 ml. of concentrated hydrochloric acid at 0–5° with 0.08 g. of sodium nitrite. After 20 minutes an excess of cold, 30% aqueous hypophosphorus acid was added, and the reaction mixture was then allowed to stand in the cold for 20 hours. Warming of the reactants on the steam-bath for 30 minutes was followed by dilution with 30 ml. of water and extraction with ether. The ether extract was washed, first with hydrochloric acid, then with water, next with 1% sodium hydroxide solution and finally again with water. Removal of ether left 30 mg. of a soft resinous material which could not be crystallized. After evaporative distillation this substance proved to have infrared absorption identical to that of the neutral products obtained from the deamination of the amino enol lactone V and from the oxidation of methyl dehydroabietate (*vide infra*). This spectrum serves to identify the substance as somewhat impure enol lactone VII, $[\alpha]_D + 163.5^\circ$ (c 2.5).

Anal. Calcd. for C₁₅H₂₂O₂: C, 79.96; H, 8.20. Found: C, 77.32; H, 8.03.

The alkaline layer above was acidified and extracted with ether. After being washed, the ether was removed leaving 240 mg. of residue which was recrystallized from ethanol, m.p. 153–156°, $[\alpha]_D + 163^\circ$ (c 0.57). This keto acid VI melted undepressed with the keto acids obtained from the oxidation of methyl dehydroabietate (*vide infra*).

Anal. Calcd. for C₁₅H₂₄O₂: C, 74.97; H, 8.39. Found: C, 75.17; H, 8.36.

The deamination of 140 mg. of the amino enol lactone V and separation into neutral and acidic fractions was carried out exactly as described above. The neutral fraction VII, 23 mg., was non-crystalline but had the same infrared ab-

sorption of the enol lactone obtained above. The acidic fraction (VI), 91 mg., was crystallized from ethanol, m.p. 154–156°, undepressed with the keto acid above.

Oxidation of Methyl Dehydroabietate (VIII).—The methyl ester, m.p. 62–63°, 3.14 g., was oxidized at 70° in 300 ml. of acetic acid with 7.8 g. of chromium trioxide in 4 ml. of water and 100 ml. of acetic acid as already described in previous oxidations. The neutral oxidation product was recrystallized from ethanol in the form of prisms, m.p. 143–144°. This substance has been shown by ultraviolet and infrared spectral comparisons and by mixed m.p. to be 1,2-dimethyl-1-carbomethoxy-7-acetyl-1,2,3,4,9,10,11,12-octahydro-9-phenanthrone (IX).⁶ Yields ranging from 17–20% of IX were obtained from a series of duplicate oxidations.

Some Esters of 2-Thenoic Acid

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Several 2-thenoic acid esters were prepared by refluxing 10 g. (0.07 mole) of the acid in an excess (125 ml.) of the required alcohol containing 5 ml. of concd. sulfuric acid. After heating for four hours, the crude ester was worked-up in the usual manner and vacuum distilled. The ethyl¹ and phenyl² esters have been reported previously.

TABLE I
ESTERS OF 2-THENOIC ACID

Ester	Yield, %	B.p. uncor.		n_D^{20}	d_4^{20}	Carbon		Hydrogen		Analyses, % Sulfur		MR _D	
		°C.	Mm.			Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd. ^a	Obsd.
Methyl	71	40	0.50	1.5420	1.2290	50.71	50.80	4.26	4.20	22.52	22.49	36.38	36.35
Ethyl	78	45	.40	1.5248	1.1620	53.84	53.88	5.16	5.00	20.50	20.60	41.03	41.18
<i>n</i> -Propyl	75	57	.45	1.5170	1.1123	56.46	56.48	5.92	6.10	18.81	18.56	45.70	46.28
Isopropyl	31	36	.05	1.5120	1.1026	56.46	56.52	5.92	5.88	18.81	18.73	45.71	46.33
<i>n</i> -Butyl	80	58	.15	1.5122	1.0859	58.69	58.64	6.57	6.56	17.38	17.31	50.32	50.93
Isobutyl	60	43	.06	1.5083	1.0751	58.69	58.54	6.57	6.67	17.38	17.38	50.35	51.12
<i>sec</i> -Butyl	32	46	.18	1.5075	1.0862	58.69	58.62	6.57	6.88	17.38	17.36	50.15	50.52
<i>n</i> -Amyl	67	63	.13	1.5071	1.0573	60.59	60.84	7.12	7.16	16.15	15.96	54.98	55.82
Tri-isoamyl	59	76	.07	1.5068	1.0593	60.59	60.91	7.12	6.93	16.15	16.26	54.93	55.60
<i>n</i> -Decyl	83	130	.13	1.4947	0.9995	67.13	67.19	9.02	8.92	11.93	11.97	78.05	78.28
Benzyl	22	98	.03	1.5720	1.1672	64.70	64.63	3.95	3.91	15.68	15.65	60.63	61.54

^a Contains the sulfide value derived from dialkyl sulfides. constant based on alkylphenyl sulfides.

Individual sums are increased by 0.56 unit using the sulfide

A total of 220 mg. of crude acidic product was isolated which melted at 120° and evolved carbon dioxide at 160°. Consequently 177 mg. of this material was heated between 120–160° until gas evolution ceased, giving a weight loss of 16 mg. A portion of this product (130 mg.) was separated into neutral and acidic fractions in the usual way. The acidic fraction (99 mg.) was crystallized, after seeding, from methanol as prisms of the keto acid VI, m.p. 154–156°, undepressed with VI from the deamination reactions above. The neutral fraction could not be crystallized but gave the infrared absorption attributed to the enol lactone VII above.

Interconversion of Enol Lactone VII and Keto Acid VI.—The neutral product, VII, (10 mg.) from the deamination of IV and V and from the oxidation of methyl dehydroabietate was refluxed for 5 minutes in 10 ml. of 5% aqueous alcoholic sodium hydroxide. After dilution of the clear solution with 50 ml. of water, the solution was acidified and extracted with ether. Crystallization of the residue from the ether solution gave prisms of the keto acid VI, m.p. 154–156°, mixed m.p. undepressed.

The keto acid (20 mg.) was refluxed in 5 ml. of acetic anhydride for 12 hours. This was diluted with 20 ml. of water and warmed for a short time, after which it was further diluted and extracted with ether. After washing and elimination of the ether, a resinous substance remained which resisted crystallization but gave infrared absorption identical to that of the enol lactone VII obtained above.

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(6) We wish to thank the Hercules Powder Company for supplying us with a sample of this diketo ester from their Experimental Station for these comparisons.

The molar refractivities of the esters are slightly higher than the calculated values.³ A similar exaltation is shown by 2-acetylthiophene⁴ although thiophene gives an optical depression.⁵ It should be noted that Vogel's quotation for the sulfide refraction value was based upon a dialkyl sulfide series. However, phenyl alkyl sulfides exhibit a consistently higher value for the sulfide constant.⁶ The "high" molar refraction values of the esters would be eliminated by using the modified sulfide constant. The esters' infrared spectra (2–35 μ) will be discussed elsewhere.

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