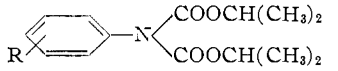
TABLE I

ISOPROPYL PHENYLIMIDODICARBOXYLATES



R	Carbamate M.p. or b.p. (mm.), °C.	Imidodicarboxylate M.p. or b.p. (mm.), °C.	Nitrogen, %[b]		Carbon, %		Hydrogen, %	
			Found	Calcd.	Found	Calcd.	Found	Calcd.
H	Not taken	82–83	5.2	5.3	63.68	63.37	7.16	7.23
3-Cl	Not taken	46–47[a]	4.7	4.7	55.92	56.09	5.94	6.06
3-CH_3	142–145 (4)	138–140(4)	4.9	5.0	65.92	64.48	7.73	7.59
3-F	60–62 (5)	69–71	5.0	4.9	59.53	59.34	6.40	6.42
4-F	85–86	59–60	4.7	4.9	59.56	59.34	6.33	6.42
4-Cl	55–57	68–69	4.3	4.7	56.10	56.09	6.10	6.06
3-Br	145–148	59.60	4.1	4.1	49.06	48.84	5.26	5.28
4-Br	Not taken	93–94	4.2	4.1	48.86	48.84	5.23	5.28
3-I	50–52	42–43	3.3	3.6	43.75	42.98	4.89	4.65
4-I	114–115	126–127	3.4	3.6	43.05	42.98	4.80	4.65

[a] Melts at 38°, resolidifies and remelts at 46–47°. [b] Kjeldahl N.

dicarboxylate as well and found it toxic, but published no further work on this series. As these compounds are relatively unknown, the synthesis and properties of some ring substituted phenylimidodicarboxylates are reported herewith.

Diels and Nawiasky[7] and Tompkins and Degering[8] obtained phenylimidodicarboxylic esters by treating alkyl phenylcarbamates with sodium and then adding alkyl chloroformates to the salt thus formed. This procedure was adapted successfully to the synthesis of ring-halogenated phenylimidodicarboxylates by treating the corresponding carbamates with finely divided sodium in ether at room temperature. Compounds containing each of the four common halogens were prepared and under these conditions no extensive reaction occurred at the halogen atom with sodium since yields of the halophenylimidodicarboxylates were better than 50%.

The method failed with β-chloroethyl phenylcarbamate, and 3-phenyl-2-oxazolidone was the only product isolated.

Although the hitherto unreported carbamates were not analyzed, their structure is established by the well-known method of their preparation and the analyses of their corresponding imidodicarboxylate derivatives. Where the phenylimidodicarboxylate was a solid, mixed melting points were taken with the corresponding carbamates. In all cases depression was observed.

Experimental

General Method for the Preparation of Isopropyl Phenylimidodicarboxylates.—The appropriate halosubstituted phenylcarbamate was prepared from the aniline and isopropyl chloroformate by the Schotten–Baumann reaction and purified either by recrystallization or distillation under reduced pressure. Sodium powder (0.1 mole) and the carbamate (0.1 mole) were stirred together at room temperature in 200 ml. of sodium-dried ether for 24 to 36 hours until all of the sodium had reacted to form the sodium salt of the carbamate by replacement of the amide hydrogen.

Isopropyl chloroformate (0.1 mole) in 50 ml. of absolute ether then was added in portions over a period of 2 hours (causing refluxing) and stirring continued for an additional 24 hours. The resulting mixture was washed with water to remove the sodium chloride that had formed, and the ether solution dried over sodium sulfate. The solvent was removed by evaporation in an air stream on the steam-bath, leaving a sirup which usually crystallized upon cooling. This was recrystallized from petroleum ether (d. 0.67–0.69), or ether ligroin, or redistilled to give the pure phenylimidodicarboxylate.

Allyl Phenylimidodicarboxylate.—The allyl phenylcarbamate was added to an equivalent amount of sodium powder as described above, and stirred for 48 hours. Half the requisite amount of allyl chloroformate was added at once, whereupon the ether commenced to boil rapidly. After 30 minutes the remainder of the chloroformate was added and the resulting mixture refluxed 24 hours and worked up. A clear colorless oil was obtained, b.p. 148–150° (5 mm.).

Anal. Calcd. for $C_{14}H_{15}NO_4$: N, 5.4; C, 64.35; H, 5.80. Found: N, 5.4; C, 64.64; H, 6.01.

2,3-Dibromopropyl Phenylimidodicarboxylate.—Allyl phenylimidodicarboxylate (0.1 mole) was dissolved in 50 ml. of glacial acetic acid and 0.2 mole of bromine was added dropwise with stirring. After the addition was complete, the mixture was stirred an additional 30 minutes and then diluted with water. An oil separated which solidified upon standing for two days. This solid was recrystallized from ether–ligroin to give colorless crystals of 2,3-dibromopropyl phenylimidodicarboxylate, m.p. 105–107°.

Anal. Calcd. for $C_{14}H_{15}Br_4NO_4$: N, 2.4; C, 28.94; H, 2.81. Found: N, 2.3; C, 26.20; H, 2.57.

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[7] O. Diels and P. Nawiasky, *Ber.*, **37**, 3682 (1904).

[8] L. Tompkins and E. Degering, THIS JOURNAL, **69**, 2616 (1947).

Triton B in Synthesis of 3-Phenylcyclohexenones

BY GORDON N. WALKER

RECEIVED FEBRUARY 21, 1955

Among the known methods of synthesis of unsaturated 3-(or 5)-phenylcyclohexanones are Knoevenagel condensation of benzaldehydes with two molecules of β-ketoester, a process which gives rise initially to dicarbalkoxy-3-hydroxy-5-phenylcyclohexanones, such as Ia,[1] and later, after treatment with a sodium alkoxide, the unsaturated ketone[2,3]; and addition of β-ketoesters to phenyl vinyl ketones or Mannich bases equivalent to such ketones,[4] which reaction also involves cyclization and furnishes 3-phenyl-6-carbethoxycyclohex-2-ene-1-ones, such as II, from which 3-phenylcyclohex-2-ene-1-ones (V) are obtained by hydrolysis and decarboxylation.

A new method for preparing V now has been found. Reaction of ethyl benzoylacetate and methyl vinyl ketone in the presence of benzyltrimethylammonium hydroxide (Triton B) in *t*-butyl alco-

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[1] P. Rabe and F. Elze, *Ann.*, **323**, 83 (1902).

[2] P. Rabe and D. Spence, *ibid.*, **342**, 352 (1905).

[3] W. Dieckmann, *Ber.*, **45**, 2689 (1912).

[4] F. C. Novello, M. E. Christy and J. M. Sprague, THIS JOURNAL, **75**, 1330 (1953). *Cf.* also the procedure of N. F. Albertson, as reported in reference 10.

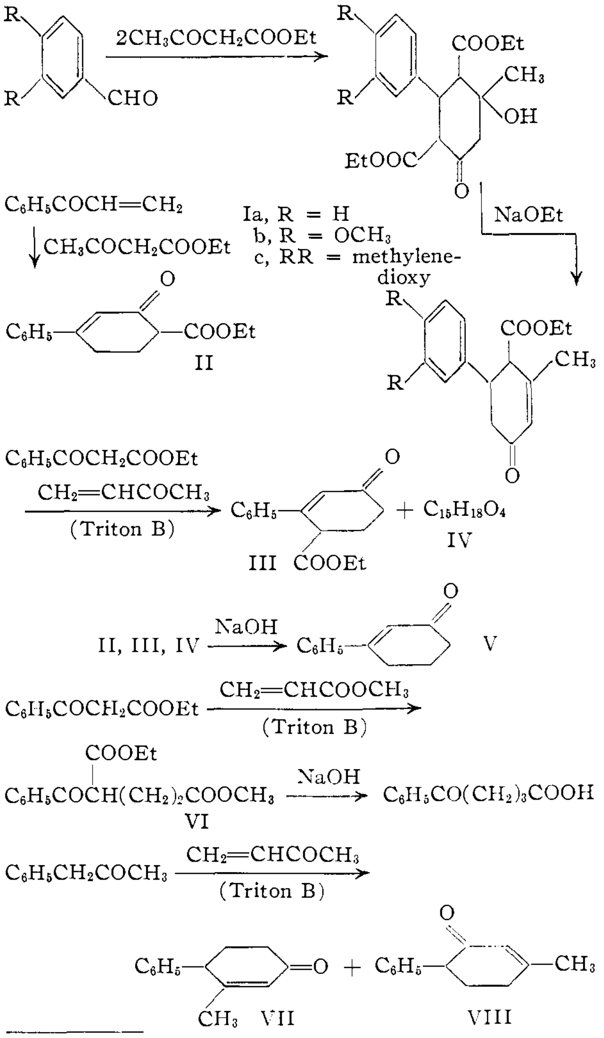
hol *and water* gave a mixture of oily material (55% yield) and a crystalline compound (21% yield). It was shown that the liquid product in all probability had structure III, as follows. The infrared spectrum of the oil had bands characteristic of enolic hydroxyl, ester and conjugated ketone groups. A single, pure 2,4-dinitrophenylhydrazone was obtained from the material in good yield, and this derivative gave analytical figures agreeing with a 2,4-dinitrophenylhydrazone derived from $C_{15}H_{16}O_3$. The oily product absorbed one mole of hydrogen in the presence of a palladium catalyst. Hydrolysis and decarboxylation of the material gave ketone V, which in turn gave the known compound 3-phenylcyclohexanone upon hydrogenation. Ketone V and its 2,4-dinitrophenylhydrazone were identical with the respective compounds prepared *via* Robinson condensation of ethyl acetoacetate with ω-dimethylaminopropiophenone hydrochloride, and hydrolysis–decarboxylation of the product II. Structure II also conceivably could arise through "abnormal" Michael reaction[5] of ethyl benzoylacetate and methyl vinyl ketone and subsequent aldol cyclization, but this process is very unlikely to have occurred under the conditions used here. Thus structure III, resulting from normal Michael reaction and aldol cyclization, appears to be justified for the oily adduct.

Compound IV, a crystalline by-product from the reaction, had formula $C_{15}H_{18}O_4$, as evidenced by analysis. The infrared spectrum showed the presence of hydroxyl, ester and unconjugated ketone groups. The compound formed a yellow mono-2,4-dinitrophenylhydrazone in which the hydroxyl and ester groups were preserved, as indicated by analysis and infrared spectrum. Unlike III, compound IV did not give an appreciable ferric chloride test and did not absorb hydrogen in the presence of 10% palladium–charcoal catalyst, even in acetic acid at 80°. The inert character of the hydroxyl group of IV under these conditions is evidence against the possibility that this group occupies a benzyl position. However, IV gave the same hydrolysis–decarboxylation product V as was obtained from III. Thus IV must be closely related to III, and may be the *cis* isomer (with respect to the phenyl and carbethoxy groups) of 3-hydroxy-3-phenyl-4-carbethoxycyclohexanone in which the hydroxyl group is held equatorially in space and is resistant to elimination. Dr. William S. Johnson very kindly suggested this explanation for compound IV, for which further evidence may be obtained in experiments now in progress.

A closely allied reaction, that of ethyl benzoylacetate with methyl acrylate, also was carried out with Triton B as catalyst, under the same conditions used in condensation of ethyl benzoylacetate with methyl vinyl ketone. Normal Michael addition resulted in formation of an oily keto-diester VI, which upon hydrolysis and decarboxylation with sodium hydroxide solution gave γ-benzoylbutyric acid, identical with material prepared by glutaroylation of benzene. The monocyanoethylation of ethyl benzoylacetate, which is very similar, has been reported.[6,7]

The reaction of phenylacetone with methyl vinyl ketone also was investigated. In this case, as in the preparation of III, there is opportunity for cyclization to occur after addition of the ketoester methylene group to the unsaturated ketone, but unlike III, where only one type of product can be formed, cyclization here can proceed in two different directions (VII and VIII). Actually the reaction led to formation of an oily product which appeared to be a mixture of VII and VIII, since the material upon distillation was found to have a b.p. range of 20°. That cyclization had occurred was shown by preparation of a mono-2,4-dinitrophenylhydrazone from this product.

Triton B also was used to advantage in condensation of veratraldehyde and piperonal with ethyl acetoacetate. These reactants do not give cyclic ketones when piperidine is employed as catalyst, but with the stronger base present, mixtures of Ib and Ic, respectively, with corresponding unsaturated cyclic ketoesters were obtained in each case. These structures were confirmed by infrared spectra, preparation of mono-2,4-dinitrophen-



Ia, R = H
b, R = OCH_3
c, RR = methylenedioxy

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(5) P. R. Shafer, W. E. Loeb and W. S. Johnson, THIS JOURNAL, **75**, 5963 (1953).

(6) N. F. Albertson, *ibid.*, **72**, 2594 (1950).

(7) C. W. Yoho and R. Levine, *ibid.*, **74**, 5597 (1952).

ylhydrazones, and, in the case of Ib, by hydrolysis–decarboxylation to the 3-aryl-5-methylcyclohex-5-ene-1-one.

Hydrogenation of the unsaturated ketoesters accompanying Ib and Ic resulted partially in formation of saturated ketoesters. However, attempts to prepare keto acids from these materials and from the hydrogenation product of III by mild alkaline hydrolysis were not promising.

Experimental[8]

Condensation of Ethyl Benzoylacetate and Methyl Vinyl Ketone.—A solution of 113.5 g. (0.59 mole) of ethyl benzoylacetate and 41.5 g. (0.592 mole) of methyl vinyl ketone in 130 ml. of *t*-butyl alcohol was treated with 108 ml. of 40% aqueous Triton B solution in one portion. The temperature rose to 60°, and the solution rapidly became dark green. The solution was stoppered and allowed to stand at room temperature for 1.5 hours. It was poured into 500 ml. of cold water. The products were extracted with ether–ethyl acetate. The organic solution was washed with three portions of cold water and was dried over magnesium sulfate. Evaporation of the solvents gave a partly crystalline residue. The components were separated by trituration with dry ether, in which the crystals were very sparingly soluble. The yield of crystalline IV, m.p. 123–127°, was 33 g. (21%). Recrystallization from methanol gave colorless crystals, m.p. 128–130°. The infrared spectrum (chf.) had peaks at 2.90, 5.80 and 5.85 μ. The material gave a very weak green ferric chloride test on standing.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.50; H, 6.86.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; yellow needles, m.p. 206–207.5°. The infrared spectrum (chf.) had peaks at 2.87 (OH), 3.00 (NH), 5.85 (bonded ester) and 6.16 μ (C=N).

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.01; H, 5.01. Found: C, 57.20; H, 5.04.

The filtrate from the trituration (described above) yielded 80 g. (55%) of yellow oil III upon evaporation of the ether. This material was partly soluble in 5% sodium hydroxide and gave a deep purple color with ferric chloride solution, and thus was evidently an enol, at least in part. The infrared spectrum (chf.) had peaks at 2.90, 5.80–5.85 (ester), 5.93 (conjugated ketone) and a weak band *ca.* 6.0 μ (conjugated double bond). The material decomposed gradually upon attempted distillation *in vacuo*, one of the products of this cleavage being ethyl benzoylacetate (identified as the 2,4-dinitrophenylhydrazone, m.p. 164–166°, mixed m.p. undepressed).

The 2,4-dinitrophenylhydrazone was obtained in 90% yield from the crude, oily product; red crystals, m.p. 168.5–170°, from ethanol–ethyl acetate. The infrared spectrum (chf.) had peaks at 3.01, 5.79 (ester) and 6.19 μ (conjugated C=N).

Anal. Calcd. for $C_{21}H_{20}O_6N_4$: C, 59.43; H, 4.75. Found: C, 59.68; H, 4.66.

Hydrolysis of III and IV.—Samples (1–2 g.) of crystalline IV and oily III were refluxed in turn with 50 ml. of 5% sodium hydroxide. Hydrolysis and decarboxylation of III was complete after one hour, while IV was more resistant and required 3 hours refluxing for complete conversion to V. The product was isolated from the cooled mixtures by ether extraction. The organic solution in each case was washed with several portions of water, and the solvent was removed by evaporation. Yields of V, from III and IV, were 85 and 95%, respectively. Compound V had m.p. 63–66° after recrystallization from ether (reported m.p. 64–65°,[4] m.p. 64.5–66°[9]). The infrared spectrum (chf.) had a sharp, intense peak at 6.00 μ. The ultraviolet spectrum had $\lambda_{max.}$ 221 mμ (log ε 4.00) and 283 mμ (log ε 4.29).

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; sparingly soluble red needles, m.p. 226–228° (lit.[7] m.p. 228–230°). The infrared spectrum (chf.) had sharp peaks at 3.01 and 6.18 μ.

Anal. Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58. Found: C, 61.40; H, 4.57.

Hydrogenation of V in the presence of 10% palladium–charcoal in ethyl acetate at room temperature afforded 3-phenylcyclohexanone, identified as the semicarbazone, m.p. 163–165° (reported m.p. 163.5–164.5,[9] m.p. 167.5–169°[10]).

The 2,4-dinitrophenylhydrazone crystallized in two different forms: yellow powder, m.p. 167–170°, from ethanol and glistening yellow needles, m.p. 176–178°, from ethanol–ethyl acetate. The mixed m.p. of the two forms was 169–172°. The reported[7] m.p. is 183–186°. The infrared spectrum (chf.) had peaks at 3.00 and 6.17 μ.

Anal. Calcd. for $C_{18}H_{18}O_4N_4$: C, 61.01; H, 5.12. Found: C, 60.80; H, 5.21.

Compound V also was prepared according to a procedure described earlier[4] and was found to be identical with material obtained from the hydrolyses described above. The 2,4-dinitrophenylhydrazone had m.p. 226–227°, undepressed on admixture with V 2,4-dinitrophenylhydrazone obtained as described above.

Hydrogenation of III and IV.—Compound III absorbed one mole of hydrogen in the presence of 5–10% palladium–charcoal catalyst in either acetic acid or ethyl acetate solvent. The product in each case, however, appeared to be a mixture, since no crystalline derivatives could be obtained. Fractional distillation of the product led to decomposition. Hydrolysis in 5% sodium hydroxide solution led to the formation of a gummy, highly insoluble polymer.

Compound IV was recovered unchanged after shaking under hydrogen in the presence of 10% palladium–charcoal catalyst in acetic acid at 80° for 2 hours.

Condensation of Ethyl Benzoylacetate and Methyl Acrylate.—A solution of 44 g. (0.229 mole) of ethyl benzoylacetate and 24 g. (0.279 mole) of methyl acrylate in 50 ml. of *t*-butyl alcohol was treated with 20 ml. of 40% Triton B solution. The temperature of the mixture rose slowly to 70° and a deep green color appeared. The mixture was allowed to stand for a half-hour, and was poured into cold water. The neutral product was isolated by extraction with ether and evaporation of the solvent, and amounted to 33 g. (52%) of yellow oil. The infrared spectrum (chf.) had bands at 5.75 and 5.94 μ. The 2,4-dinitrophenylhydrazone obtained from this material did not crystallize.

Hydrolysis.—The crude product (33 g.) from the preceding experiment was refluxed with 200 ml. of 20% sodium hydroxide solution for 2 hours. The cooled solution was diluted to one liter, filtered, and acidified with hydrochloric acid; carbon dioxide was evolved during the addition of the acid. The mixture was chilled, and the product was collected, washed with water, and air-dried; yield 23.7 g. of crystals, m.p. 92–109°. Recrystallization from cyclohexane–ethyl acetate afforded 18 g. (78%) of crystals, m.p. 125–127°, raised to 128–130° on further recrystallization. The mixed m.p. with authentic γ-benzoylbutyric acid was 128–130°.

Condensation of Phenylacetone and Methyl Vinyl Ketone.—A solution of 16.5 g. (0.123 mole) of phenylacetone and 9.7 g. (0.138 mole) of methyl vinyl ketone in 25 ml. of *t*-butyl alcohol was treated with 18 ml. of 40% Triton B solution. The temperature rose to 80° and the mixture became bright red. The solution was allowed to stand for a half-hour, and was poured into cold water. The neutral product was isolated as usual (23 g. of red oil). Distillation *in vacuo* gave 9.1 g. (40%) of pale yellow oil, b.p. 139–160° (2 mm.). **The 2,4-dinitrophenylhydrazone** prepared from this material crystallized partly on long standing; recrystallization of the solid fraction from ethanol-ethyl acetate gave orange plates, m.p. 162–164°.

Anal. Calcd. for $C_{19}H_{18}O_4N_4$: C, 62.29; H, 4.95. Found: C, 62.09; H, 5.13.

Condensation of Veratraldehyde and Ethyl Acetoacetate.—A solution of 30.7 g. (0.185 mole) of veratraldehyde and 47.6 g. (0.367 mole) of ethyl acetoacetate in 60 ml. of ethanol was treated with 20 ml. of 40% Triton B solution. The solution was allowed to stand 20 days at room tempera-

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[8] Melting points are corrected. I am indebted to Dr. William C. Alford and his staff for analytical data and to Mrs. Iris Siewers and Miss Fleur Bateman of the Instrument Laboratory for spectra mentioned herein.

[9] G. F. Woods and I. W. Tucker, THIS JOURNAL, **70**, 2174 (1948).

[10] W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, *ibid.*, **75**, 4999 (1953).

ture. The red solution was diluted with 300 ml. of water and 300 ml. of ether, and, after shaking, the layers were separated. The organic layer was extracted with three portions of 5% sodium hydroxide solution. Acidification of the combined alkaline solutions resulted in separation of the products, which were isolated by extraction with ether–ethyl acetate. Evaporation of the dried organic solutions gave 40 g. of crude product, which crystallized slowly (2 weeks) at ice temperature. Trituration with ether afforded 10.5 g. of colorless crystals (Ib), m.p. 135–139°, raised to 138.5–140.5° by recrystallization from ethanol. The infrared spectrum (chf.) had peaks at 2.85 (OH), 5.73 (ester), and 5.81 μ (ketone). The compound gave a faint green color with ferric chloride and was slowly soluble in 5% sodium hydroxide solution.

Anal. Calcd. for $C_{21}H_{28}O_8$: C, 61.75; H, 6.91. Found: C, 61.63; H, 6.96.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; bright yellow, fine needles, m.p. 199–201° dec. The infrared spectrum of this derivative (chf.) had peaks at 2.85 (OH), 3.00 (NH), 5.75 (unbonded ester), 5.85 (bonded ester) and 6.16 μ (unconjugated C=N).

Anal. Calcd. for $C_{27}H_{32}O_{11}N_4$: C, 55.10; H, 5.48. Found: C, 55.53; H, 5.56.

The filtrate from the trituration of Ib gave, upon evaporation of the solvents, 25 g. of very viscous orange oil which eventually set to a hard glass and did not crystallize. This material gave a deep purple color with ferric chloride, and was soluble in dilute alkali. Evidently it was an impure mixture of isomers of unsaturated cyclic ketoesters. **The 2,4-dinitrophenylhydrazone** obtained from this material had m.p. 197–199° after recrystallization from ethyl acetate; the mixed m.p. with the 2,4-dinitrophenylhydrazone of Ib was 181–185° (depressed). The infrared spectrum of this derivative had peaks at 3.01 (NH), 5.77 (ester) and 6.18 μ (C=N).

Anal. Calcd. for $C_{27}H_{30}O_{10}N_4$: C, 56.84; H, 5.30. Found: C, 57.13; H, 5.50.

3-(3′,4′-Dimethoxyphenyl)-5-methylcyclohex-5-ene-1-one.—Hydrolysis and decarboxylation of both Ib and the glassy enol obtained with it, in 5% sodium hydroxide (reflux) for one hour resulted in each case in formation of neutral, viscous oil. The same **2,4-dinitrophenylhydrazone** was obtained from both products as dense, glittering, deep red crystals from ethyl acetate, m.p. 207–209°.

Anal. Calcd. for $C_{21}H_{22}O_6N_4$: C, 59.15; H, 5.20. Found: C, 58.95; H, 5.33.

2,4-Dicarbethoxy-3-(3′,4′-dimethoxyphenyl)-5-methylcyclohexanone.—Hydrogenation of 10.3 g. of the glassy enol obtained with Ib, in the presence of 2 g. of 10% palladium-charcoal catalyst in 200 ml. of acetic acid at 80° for 1.5 hours resulted in the formation of 5.2 g. of neutral oil. The remainder of the material obtained after this reaction was a viscous, brown, alkali-soluble gum. **The 2,4-dinitrophenylhydrazone** was prepared from the neutral fraction and was recrystallized from ethanol–ethyl acetate; bright yellow crystals, m.p. 187–189°. The infrared spectrum of the derivative (chf.) had peaks at 3.02, 5.76 (ester) and 6.17 μ.

Anal. Calcd. for $C_{27}H_{32}O_{10}N_4$: C, 56.64; H, 5.63. Found: C, 56.49; H, 5.62.

Condensation of Piperonal and Ethyl Acetoacetate.—Reaction of 36.5 g. (0.243 mole) of piperonal and 63.5 g. (0.489 mole) of ethyl acetoacetate was carried out in the presence of 22 ml. of 40% Triton B in 60 ml. of ethanol. After 7 days standing, 19.7 g. of crystalline Ic, m.p. 148–150°, and 22 g. of crude, glassy, orange enol were obtained upon treating the mixture in the same way as described for the veratraldehyde products. Further recrystallization of Ic (ethanol) did not raise the melting point. The infrared spectrum (chf.) had peaks at 2.85, 5.73 and 5.80 μ.

Anal. Calcd. for $C_{20}H_{24}O_8$: C, 61.21; H, 6.2. Found: C, 60.93; H, 6.6.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate; yellow-orange needles, m.p. 220–222°. The infrared spectrum (chf.) had peaks at 2.85–2.90, 3.02, 5.75, 5.85 and 6.16 μ.

Anal. Calcd. for $C_{26}H_{28}O_{11}N_4$: C, 54.54; H, 4.93. Found: C, 54.59; H, 5.05.

The glassy material, obtained by evaporation of the filtrates after trituration, gave a deep red-purple color with ferric chloride. Two different orange **2,4-dinitrophenylhydrazones** were obtained by fractional crystallization (ethyl acetate) of the crude derivative from this product. The first one, m.p. 204–206°, evidently contained one ester group and a hydroxyl group, as evidenced by infrared spectrum (peaks at 2.8–2.85, 2.98, 5.77 and 6.16 μ) and analysis.

Anal. Calcd. for $C_{23}H_{24}O_9N_4$: C, 55.20; H, 4.83. Found: C, 55.21; H, 4.86.

The second fraction had m.p. 223–225° dec. after numerous recrystallizations; this material was less soluble than the first fraction and had a deeper orange color. A satisfactory analysis could not be obtained. The infrared spectrum was very similar to that of the first derivative except that there was no hydroxyl band (2.85 μ) present, and thus dehydration was indicated.

Hydrogenation of the glassy enol mixture (palladium) resulted in absorption of less than one mole of hydrogen, and no pure derivatives could be obtained from the neutral product. Hydrolysis of Ic (5% alkali) gave a neutral, ketonic product, but no crystalline derivatives could be obtained from this material.

LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS
NATIONAL HEART INSTITUTE
NATIONAL INSTITUTES OF HEALTH
BETHESDA 14, MARYLAND

COMMUNICATIONS TO THE EDITOR

THE STRUCTURE OF FRIEDELIN. DEGRADATIVE STUDIES

Sir:

The terpenoid ketones, friedelin and cerin (α-hydroxy-friedelin) belong to a new class of pentacyclic triterpenes,[1] differing from the known β-amyrin, α-amyrin and lupeol types. We record in this and the following communication the experimental findings which have revealed the structures of these triterpenes.

The starting point for this work was the assumption that friedelin possesses partial carbon skeleton I (1,8-dimethylpicene formed by dehydrogenation[2]) and the information that the unit $-\underset{|}{\mathrm{CH}}-\underset{|}{\mathrm{CH}}-\mathrm{CO}-\mathrm{CH_2}-\mathrm{CH_2}-$ is present (indicated by the preparation of the C_{29} α-diketone, norfriedelendione[3]). These conditions limit the oxo function to two positions, C_1 and C_3. Proof of the location of oxygen at C_3 and a methyl at C_4 was obtained in several ways, including: (1) three-step oxidation of friedelin to a C_{23}, six-membered lactone (II), m.p. 228–235°, $[\alpha]^{25}\mathrm{D}$ +9.6°,[4] infrared max. 1740 cm.$^{-1}$. Found: C, 80.83; H,

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[1] N. L. Drake and R. P. Jacobsen, THIS JOURNAL, **57**, 1570 (1935).

[2] N. L. Drake and W. T. Haskins, *ibid.*, **58**, 1684 (1936).

[3] L. Ruzicka, O. Jeger and P. Ringnes, *Helv. Chim. Acta*, **27**, 972 (1944).

[4] All rotations in chloroform solution (*C*, *ca.* 1.0).