minutes, and the mixture again heated to complete the reaction. Sodium chloride was removed by filtration and toluene by distillation under diminished pressure. The residual liquid was subjected to distillation and 30.6 g. (85% yield) of 1-(*p*-tolylmercapto)-2-propanone was obtained as a pale yellow liquid boiling over the range 133–135° (7–9 mm.).

Preparation of 1-(*m*-Tolylmercapto)-2-propanone.—This compound was prepared by the method outlined for the *p*-isomer, but was obtained in slightly lower yield (78%) as a pale yellow liquid boiling at 142° (8 mm.).

Preparation of 1-(*o*-Tolylmercapto)-2-propanone.—By use of the same general procedure 1-(*o*-tolylmercapto)-2-propanone was obtained in 84% yield as a pale yellow liquid boiling at 138° (8 mm.).

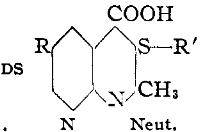
Preparation of 5-Methylisatin.[4]—This compound was prepared by the procedure outlined in "Organic Syntheses," and the product was purified by recrystallization from glacial acetic acid.

Preparation of 3-(*p*-Tolylmercapto)-4-quinaldinecarboxylic Acid.—Seventeen and one-tenth grams (0.116 mole) of isatin was dissolved in 200 cc. of thirty-three per cent. aqueous potassium hydroxide solution, and 20.95 g. (0.116 mole) of 1-(*p*-tolylmercapto)-2-propanone was added. The resulting mixture was heated under reflux on the steam-bath for eight hours, boiled with Norite and filtered. The clarified solution was poured over an equal volume of ice and made definitely acidic by the addition of acetic acid. The cream colored solid was dissolved in potassium hydroxide solution and again treated with activated charcoal. The solution was cooled in ice and made barely acidic by the addition of acetic acid. The 3-(*p*-tolylmercapto)-4-quinaldinecarboxylic acid separated as a light cream-colored precipitate (75% yield). Dried over anhydrous calcium chloride, the product retained two molecules of water of hydration (as indicated by the analytical data for nitrogen content) which were removed by drying in a vacuum desiccator over phosphorus pentoxide. The product melted with decomposition at 274°.

The remaining 3-tolylmercaptocinchoninic acids were formed in essential accordance with this general procedure. Table I contains the data on these preparations.

Table I

3-Tolylmercaptocinchoninic Acids



R—	R'—	Yield, %	M. p., °C. (cor.)	N anal., % found[a]	Neut. equiv. found[b]
H	*p*-Tolyl	75	274	4.52	316
H	*m*-Tolyl	90	258	4.48	313
H	*o*-Tolyl	60	278	4.41	311
CH_3	*p*-Tolyl	90	275	4.27	323
CH_3	*m*-Tolyl	70	260	4.30	326
CH_3	*o*-Tolyl	66	266	4.34	328

[a] Calcd.: N, 4.53 for R = H; N, 4.33 for R = CH_3. [b] Calcd.: neut. equiv., 309 for R = H; neut. equiv., 323 for R = CH_3.

Summary

1. Pfitzinger's method has been extended to include the utilization of the tolylmercaptopropanones in the synthesis of six substituted quinoline acids from isatin and 5-methylisatin, respectively.

Atlanta, Georgia Received September 3, 1946

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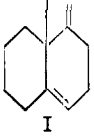
[4] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 321.

[Contribution from the Bureau of Animal Industry, Agricultural Research Administration, United States Department of Agriculture]

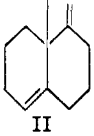
The Synthesis of Condensed Ring Compounds. XV.[1] A New 9-Methyloctalone[2]

By Adam M. Gaddis and Lewis W. Butz

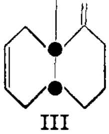
Two 9-methyloctalones have previously been prepared and partly characterized, the position of the carbon–carbon double bond being still unknown.[3] The probable structures are 10-methyl-4-naphthiten-1-one (I) and 10-methyl-5-naphthiten-1-one (II). We now report on a third 9-methyloctalone which was first prepared by Nudenberg.[4] The position of the carbon–carbon double bond in this ketone also remains undetermined. The compound is probably *cis*-10-methyl-7-naphthiten-1-one (III).



I



II



III

When 1,3-butadiene and an excess of 1-methyl-1-cyclohexen-6-one are held at 200° for about forty hours and the resulting mixture is distilled, about 80% of the methylcyclohexenone is recovered unchanged and a higher boiling ketone is obtained in about 30% yield calculated on the methylcyclohexenone consumed. This product has the composition and properties of compound III or an isomer with the C=C bond in another position. It appears to consist, at least chiefly of one isomer for several derivatives were prepared in high yield and adsorption and elution of the 2,4-dinitrophenylhydrazone, employing a column of alumina, indicated a single substance.

Controlled catalytic hydrogenation gave a known 9-methyldecalone, probably the *cis* isomer.[5] The identity was established by the constants of the dihydroketone and its derivatives and by direct comparison of the 2-benzal-9-methyl-1-decalone by melting point of the mixture

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[1] For the preceding paper see *J. Org. Chem.*, **8**, 509 (1943).

[2] This work was supported by an allotment from the Special Research Fund (Bankhead–Jones Act of June 29, 1935). Not copyrighted.

[3] Plentl and Bogert, *J. Org. Chem.*, **6**, 669 (1941).

[4] Nudenberg and Butz, This Journal, **65**, 1436 (1943).

[5] Johnson, *ibid.*, **65**, 1317 (1943).

with an authentic specimen.[6] The methyloctalone is therefore a 10-methylnaphthiten-1-one and is *cis* if the methyldecalone which it yields on hydrogenation is *cis*. This work constitutes further evidence that the Diels–Alder reaction gives *cis*-adducts and furnishes the first evidence of configuration of product in an addition to a monoketone. Conversely, if the principle of *cis*-addition be taken as established,[6a] it furnishes additional evidence for the configuration assigned[5] to the methyldecalone.

The position of the C=C bond has not yet been established. In view of the reaction of formation it is probably at position 7 as shown in formula III, but isomerization under the conditions of formation is a possibility. Non-correspondence of the melting points of the oxime (123.2–125°) and the semicarbazone (224.8–225°)[4] with those of either of the compounds of Plentl and Bogert[3] (Ketone A: oxime, 105°; semicarbazone, 228–229°. Ketone B: oxime, 120°; semicarbazone, 168°) excludes I and II as likely structures.

Two carbinols were prepared from the methyloctalone, a 1,10-dimethylnaphthiten-1-ol by reaction with methylmagnesium iodide and a 1-ethynyl-10-methylnaphthiten-1-ol by reaction with sodium acetylide.

Experimental[7]

***cis?*-10-Methyl-7?-naphthiten-1-one.**—Thirty grams of 1-methyl-1-cyclohexen-6-one, b. p. 63–69° (14 mm.), $n^{20}\text{D}$ 1.4855, from 1-methylcyclohexene and selenium dioxide and purified by a previous heating with butadiene,[8] 6 g. (10 ml.) of 1,3-butadiene, and a few crystals of hydroquinone were sealed into a no. 8640 Pyrex tube about 20 mm. in diameter which had been filled with carbon dioxide (nitrogen was sometimes used). Four tubes so charged were held at 200° for thirty-eight hours, the contents of all were combined and worked up together. Distillation gave 94.8 g. of methylcyclohexenone and 9.7 of methylnaphthitenone, boiling at 58–65° (0.4 mm.), collected in three fractions, $n^{20.4}\text{D}$ 1.5031, 1.5045 and 1.5078. About 100 g. of such material was collected and used for the preparation of derivatives and an investigation of the possibilities of conversion to condensed tetracyclic compounds.[9] A portion of this was analyzed without further purification.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.8. Found: C, 80.5; H, 10.0.

It gave, by the Iddles[10] procedure, 89.3% of 2,4-dinitrophenylhydrazone, which was not resolved in petroleum ether solution on a column of alumina.

The ketone in ethanol was added to a solution of two equivalents of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid at 45°. It was immediately allowed to cool to room temperature, then stood overnight, was filtered, washed with 2 *N* hydrochloric acid and water, and dried at 100°. Eleven mg. in 40 ml. of a fraction from petroleum (Skellysolve "B," distilled, washed with sulfuric acid and aqueous potassium permanganate solution, dried and redistilled, b. p. 68–69°) was poured onto a 6 × 460 mm. column of alumina (Merck according to Brockmann). The yellow band was washed down to the bottom of the column with about 850 ml. of the Skellysolve "B." No separation occurred. Since mixtures of 2,4-dinitrophenylhydrazones can sometimes be separated by this procedure,[8,11] homogeneity of the methylnaphthitenone is indicated. The use of hydrochloric acid in the preparation of the dinitrophenylhydrazone decreases the value of this evidence somewhat, for it must be conceded that a mixture of isomeric octalones might yield one isomer under the conditions.

Redistillation of 11.3 g. of the ketone gave 9.8 g., b. p. 58–59° (0.1 mm.), two cuts equal in weight $n^{19.4}\text{D}$ 1.5043 and $n^{19}\text{D}$ 1.5051.

This methylnaphthitenone can be stored for a long time without much decomposition. After fourteen months in the refrigerator, 9.3 g. was twice redistilled to give 7.2 g., b. p. 63–65° (0.5 mm.), $n^{20.6}\text{D}$ 1.5040.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.5; H, 9.8. Found: C, 80.3; H, 9.9.

By the Iddles method,[10] this gave 92.6% of 2.4-dinitrophenylhydrazone.

1-Methyl-1-cyclohexen-6-one from the semicarbazone of 2-hydroxy-2-methylcyclohexanone[8] was treated three times with butadiene under the conditions described. From 93.8 g. of methylcyclohexenone, $n^{20}\text{D}$ 1.4847–1.4866, 20.6 g. of methylnaphthitenone was obtained. Since 45.6 g. of methylcyclohexenone was recovered, the yield was 42%. This methylnaphthitenone gave the same yield of 2,4-dinitrophenylhydrazone as the batches prepared from the methylcyclohexenone from 1-methylcyclohexene and this 2,4-dinitrophenylhydrazone also appeared homogeneous (no separation on alumina).

The 2,4-Dinitrophenylhydrazone of the Methylnaphthitenone.—A mixture of 0.39 g. of 2,4-dinitrophenylhydrazine, 0.5 g. of methylnaphthitenone (36% excess) and 25 ml. of ethanol was brought to boiling, 0.5 ml. of concentrated hydrochloric acid was added, and boiling was continued for five minutes. After slow cooling, filtration, and washing three times with cold ethanol, 90.2% was obtained with m. p. 144–158°. Repeated recrystallization from ethanol, ethyl acetate and ethyl acetate–methanol gave the 2,4-dinitrophenylhydrazone, m. p. 158.6–162.4°.

Anal. Calcd. for $C_{17}H_{20}N_4O_4$: C, 59.3; H, 5.85; N, 16.3. Found: C, 59.4; H, 6.1; N, 16.3.

***cis?*-9-Methyl-1-decalone and 2-Benzal-9,10-*cis?*-9-methyl-1-decalone.**—A palladium–calcium carbonate catalyst[12] (0.73 g.) was covered with 50 ml. of ethanol and hydrogenated. Three grams of methylnaphthitenone in 11 ml. of ethanol was then added and the mixture was shaken in hydrogen until 0.95 of the calculated quantity had been taken up. Filtration of the catalyst and removal of the ethanol by distillation through a column gave 2 g. of *cis?*-9-methyldecalone, b. p. 72–73° (0.8 mm.), $n^{20.6}\text{D}$ 1.4895; 2,4-dinitrophenylhydrazone, m. p. 162.4–165.2°; 2-benzal derivative, m. p. 102.5–104.5°, mixture with authentic specimen[5,6] m. p. 102.5–104.5°.

Oxime of the Methylnaphthitenone.—Two grams of ketone in 15 ml. of methanol with 2.5 g. of hydroxylamine hydrochloride and 2.5 g. of sodium acetate in 7.5 ml. of warm water gave an immediate precipitate which, after standing an hour, was filtered, washed with water, and dried; 1.8 g. (86%). After recrystallization from methanol and purified Skellysolve "B," the oxime melted at 123.2–125°.

Anal. Calcd. for $C_{11}H_{17}NO$: N, 7.8. Found: N, 7.9.

1,10-Dimethyl-5,10-*cis?*-7?-naphthiten-1-ol.—Addition of 10.6 g. of methylnaphthitenone in 50 ml. of ether, during one and a quarter hours, to the Grignard reagent from 2 g. of magnesium and 12 g. of methyl iodide in 100 ml. of ether, refluxing for three hours on one day and one

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(6) We are indebted to Dr. W. S. Johnson for sending us some of the benzalmethyl-*cis*-decalone prepared in his Laboratory.

(6a) Alder and Stein, *Angew. Chem.*, **50**, 510 (1937).

(7) All melting points are corrected. Analyses by Arlington Laboratories, Fairfax, Virginia.

(8) Butz, Davis and Gaddis, *J. Org. Chem.*, in press.

(9) See paper XVI.

(10) Iddles, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 102 (1939).

(11) It was possible to separate a mixture of the 2,4-dinitrophenylhydrazones of the methylnaphthitenone and the corresponding methyldecalone by this method.

(12) Busch and Stöve, *Ber.*, **49**, 1064 (1916).

hour the next, decomposing with 100 ml. of saturated ammonium chloride solution, and working up in the usual manner gave 10.7 g. (91%) of crude carbinol boiling at 76–84° (0.7 mm.). This thrice redistilled gave 6 g., b. p. 77–78° (0.3 mm.), $n^{20.6}$D 1.5150.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 80.5; H, 11.2; hydrogenation, Adams catalyst, 1.1 double bonds.

Allophanate.—One gram of dimethylnaphthitenol and 120 ml. of a solution of 9 equivalents of cyanic acid in ether were mixed and let stand one day in refrigerator and one day at room temperature. Only a small amount of solid precipitated. Evaporation of the ether, extraction of the residue with benzene, evaporation of the benzene from the extract, and crystallization of the residue from methanol gave 0.5 g. of product, m. p. 171–172.6° (dec.). Additional crystalline material, 0.3 g., m. p. below 135°, which was not further investigated, was obtained from the residue from the methanol mother liquor with Skellysolve "B"–ether. Repeated recrystallization of the main fraction from methanol and finally from methanol containing 10% of benzene gave a dimethylnaphthitenyl allophanate, m. p. 178.8–179.6° (dec.).

Anal. Calcd. for $C_{14}H_{22}N_2O_3$: C, 63.1; H, 8.3; N, 10.5. Found: C, 63.2; H, 8.5; N, 10.6.

1-Ethynyl-10-methyl-5,10-*cis?*-7?-naphthiten-1-ol.—A solution of sodium acetylide was prepared by saturating about 600 ml. of liquid ammonia with acetylene which had been passed through sulfuric acid and over potassium hydroxide, dissolving 5.7 g. of sodium in the liquid ammonia–acetylene, and then passing acetylene in for twenty minutes more. Sixteen grams of methylnaphthitenone in 50 ml. of ether was dropped into the sodium acetylide solution during forty-five minutes, the mixture was stirred for four hours, and let stand overnight with evaporation of the ammonia. Addition of ice, ether and benzene to the residue, acidification to litmus with acetic acid, separation of the ether–benzene solution, extraction of the aqueous part with ether, washing the combined extracts with sodium bicarbonate solution, then with saturated sodium chloride solution, drying over sodium sulfate, evaporation of solvents, and distillation gave 1.8 g. of unchanged methylnaphthitenone and 14.5 g. (90%) of crude carbinol, b. p. 85–94° (0.6 mm.), which twice redistilled gave ethynylmethylnaphthitenol, 12 g., b. p. 76–78° (0.3 mm.), $n^{19.6}$D 1.5275.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 82.1; H, 9.5.

This carbinol gives a pinkish-white precipitate with silver nitrate in ammonium hydroxide–methanol. No formation of water was seen when the carbinol was heated alone at 275° or with iodine at 200°. After heating under these conditions, all of the material distilled (b. p. about 193° (193 mm.) and b. p. 135–139° (13 mm.) respectively). The refractive index was not changed.

Summary

10-Methyl-*cis?*-7?-naphthiten-1-one has been prepared from butadiene and 1-methyl-1-cyclohexen-6-one. Two 1-alkyl-1-carbinols were prepared from the ketone.

BELTSVILLE, MARYLAND RECEIVED SEPTEMBER 13, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Acylations of Esters with Esters to Form β-Keto Esters Using Sodium Amide[1,2]

BY JOSEPH C. SHIVERS, MARCUS L. DILLON AND CHARLES R. HAUSER

The acylation of esters with esters to form β-keto esters has generally been effected by sodium alkoxides[3] or, when these reagents fail, by sodium[3] or potassium[4] triphenylmethide. Relatively few of these condensations have previously been effected by sodium or potassium amide. Sodium amide has been found more effective than sodium alkoxides for the analogous acylations[5] or carbethoxylations[6] of ketones, and, when it is applicable, sodium amide should also be more effective for the acylation of esters. Indeed, the amide ion should be even more effective than the triphenylmethide ion because it is a stronger base. However, the application of sodium amide to the acylation of esters is limited by the fact that the amide ion often converts the ester to the corresponding amide[7] instead of to the ester anion, which is the reactive intermediate in the condensation. Nevertheless, on the basis of a recent study[8] on the influence of structure of esters on the proportions of ester anion and amide formed, it has become possible to extend considerably the number of acylations of esters using sodium amide. Various self and mixed-ester condensations using this reagent are described in the present investigation.

Self-condensations.—Preliminary experiments with *n*-amyl acetate indicated that the condensations were best effected by adding the ester, in 10% excess, to sodium amide in liquid ammonia, replacing the ammonia by ether and refluxing the mixture, although other conditions also produced satisfactory yields in certain cases.

Sodium amide (0.3 mole) in 300 ml. of anhydrous ammonia was prepared as described previously[5,6] in a one-liter three-necked round-bottomed flask equipped with a mercury-sealed stirrer, dropping funnel and condenser having a tube of drierite. With the drying tube removed, 0.33 mole of the ester in an equal volume of dry ether was

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(1) Paper XXXVII on "Condensations"; paper XXXVI, THIS JOURNAL, 68, 2647 (1946).

(2) This investigation was supported in part by a grant from the Duke University Research Council.

(3) See Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, New York, N. Y., 1942, Vol. I, Chap. IX.

(4) Levine, Baumgarten and Hauser, THIS JOURNAL, 66, 1230 (1944).

(5) Adams and Hauser, *ibid.*, 66, 1220 (1944); Levine, Conroy, Adams and Hauser, *ibid.*, 67, 1510 (1945).

(6) Levine and Hauser, *ibid.*, 66, 1768 (1944).

(7) For a discussion of four types of reactions that esters may exhibit with bases, see Hauser, Shivers and Skell, THIS JOURNAL, 67, 409 (1945).

(8) Hauser, Levine and Kibler, *ibid.*, 68, 26 (1946).