reaction mixture was neutralized with 20 cc. of a saturated solution of sodium carbonate, washed with water, dried over anhydrous sodium sulfate, and the solvent removed by distillation.

Gas chromatographic analysis of the residue on a diethylene adipate column[20] indicated the product was a 34:66 mixture of isomers. The residue was distilled and 49.5 g. (77%) of product was collected at 116–123° (19 mm.), $n^{25}\text{D}$ 1.5027.

Anal. Calcd. for $C_9H_{16}OS$: C, 62.74; H, 9.36; S, 18.61. Found: C, 62.83; H, 9.86; S, 18.24.

The isomers were separated on a 3 × 45 cm. neutral alumina column by elution with hexane. The first fraction collected was the minor constituent and was shown to be the S-equatorial isomer (Vb) by n.m.r. analysis (deuteriochloroform) which showed triplets at −183 c.p.s. (S–CH_2) and −248 c.p.s. (O–CH_2). The second isomer collected (S-axial, Va) which represented 66% of the total product showed n.m.r. triplets (deuteriochloroform) at −181 c.p.s. (S–CH_2) and −252 c.p.s. (O–CH_2).

7,7,9-Trimethyl-1,4-oxathiospiro[4.5]decane (VI).—The procedure described in V was used starting with 3,3,5-trimethylcyclohexanone and mercaptoethanol in benzene with *p*-toluenesulfonic acid as the catalyst. The product was collected in 45% yield at 118–131° (19 mm.). The isomers were separated on neutral alumina using hexane for elution. The first isomer collected (VIa) showed n.m.r. triplets (deuteriochloroform) at −178 c.p.s. (axial S–CH_2) and −251 c.p.s. (equatorial O–CH_2). The second isomer (VIb) showed triplets at −180 c.p.s. (equatorial S–CH_2) and −248 c.p.s. (axial O–CH_2).

Anal. Calcd. for $C_{11}H_{20}OS$: C, 65.95; H, 10.06; S, 16.00. Found: C, 65.40; H, 9.93; S, 15.70.

The progress of the reaction was followed by withdrawing and immediately neutralizing samples of the reaction mixture. These were taken at 5-min. intervals starting with the addition of catalyst to the refluxing solution of ketone and mercaptoethanol. Gas chromatographic analysis revealed after 10-min. reaction time a ratio of 68:32 in favor of the O-equatorial isomer (VIa). This gradually changed (seven determinations until stabilizing at 76:24 after 100 min.) and remained unchanged for the next 20 hr.

7-*t*-Butyl-1,4-oxathiospiro[4.5]decane (VII).—This was prepared according to the procedure described in V from 3-*t*-butylcyclohexanone[21] and mercaptoethanol. The product was collected in 43% yield at 140–142° (11 mm.). Column chromatography yielded the O-equatorial isomer (VIIa) with n.m.r. triplets (carbon tetrachloride) at −176 (S–CH_2) and −246 c.p.s. (O–CH_2), while the S-equatorial isomer (VIIb) gave proton signals at −178 and −243 c.p.s., respectively.

Anal. Calcd. for $C_{12}H_{22}OS$: C, 67.25; H, 10.35; S, 14.93. Found: C, 67.25; H, 10.40; S, 14.90.

Analysis of the progress and equilibrium of the reaction was according to the procedure used in VI. The ratio changed from 76:24 in favor of the O-equatorial isomer (1-min. reaction time) to 82:18 after 18 hr. reflux. Gas chromatographic analysis was difficult due to overlap; in this case a retention time difference of about 2 min. was found, necessitating an approximation of the ratios.

Equilibrations.—The hemithioketals V and VI were refluxed with a 2.5 mol. equiv. of boron trifluoride in ether (100 parts) until equilibrium was reached as shown on gas chromatographic analysis. A mixture of the isomers of 7-methyl-1,4-oxathiospiro[4.5]decane (VI) and also an ether solution of the pure oxygen-equatorial isomer were both equilibrated to a 76:24 ratio infavor of the oxygen–equatorial isomer.

7,7,9-Trimethyl-1,4-oxathiospiro[4.5]decane (VI) and the pure isomer VIa were equilibrated to give in both cases a 79:21 ratio in favor of the O-equatorial isomer (VIa).

Acknowledgment.—The author wishes to thank Dr. E. L. Eliel for many helpful discussions, Mr. Harry Lott and Dr. Reynold T. Iwamoto for use of the Perkin-Elmer 421, and Mr. Donald Thompson and Mr. George MacDonald for technical assistance. Partial support was received from The University of Kansas General Research Fund.

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[20] LAC-446 on Chromosorb P (F and M Scientific Corp.).

[21] C. Djerassi, E. Warawa, R. E. Wolff, E. J. Eisenbruan, *J. Org. Chem.*, **25**, 917 (1960).

Addition of Grignard Reagents to 1,3-Dimesitoylbenzene[1]

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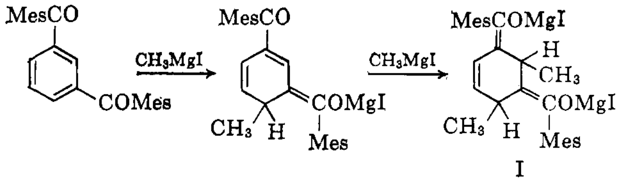
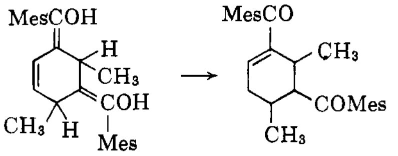
1,3-Dimesitoylbenzene reacts with two moles of methylmagnesium iodide; the product has been identified as a mixture of stereoisomeric 2,4-dimesitoyl-3,5-dimethylcyclohexenes.

Conjugate addition of Grignard reagents to hindered diaryl ketones involves nucleophilic attack on a benzene ring.[2] It would be expected that vulnerability of the ring to such attack would be increased by a second ketone group, especially if it were in a position *meta* to the first. To test this idea we have studied the behavior of 1,3-dimesitoylbenzene toward the methyl and benzyl Grignard reagents. Reaction should occur initially at the 4-position; a second mole of the reagent would be expected to react readily with the adduct since the ring involved would have lost its aromatic character. Reaction with the methyl reagent would then take the following course.



I

Ketonization of the dienol produced by hydrolysis of adduct I might be expected to yield 2,4-dimesitoyl-3,5-dimethylcyclohexene (II).



II

The product, isolated in 59% yield, proved to be a mixture of stereoisomers of ketone II. It was not possible to isolate all of the isomers, but chromatography over alumina yielded a high melting, dimorphic isomer, m.p. 159–160° and 174.5–175.5°. Analyses of both the recrystallized mixture of isomers and the high melting isomer were consistent with the composition of $C_{28}H_{34}O_2$.

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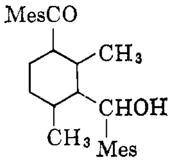
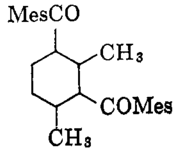
[1] This research was supported in part by grant no. NSF-G22092 from the National Science Foundation.

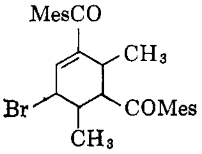
Reaction of *m*-dimesitoylbenzene with benzylmagnesium chloride also gave a diadduct which is assigned a structure analogous to II. Structural work, however, has been carried out on II since the presence of benzyl groups complicated both spectral and chemical studies.

Spectral evidence is in accord with structure II. Infrared spectra show absorption characteristic of a saturated alkyl mesityl ketone, an α,β-unsaturated ketone, and a conjugated carbon–carbon double bond. Nuclear magnetic resonance spectra show the presence of a β-proton of an α,β-unsaturated carbonyl group adjacent to a methylene group (triplet, 3.41 τ) and two methyl groups attached to saturated carbon atoms (doublets, 8.77 and 8.87 τ).

Reduction of ketone II with lithium aluminum hydride[2] followed by oxidation of keto alcohol III to diketone IV confirms the presence of both a conjugated and a nonconjugated ketone. The saturated diketone IV shows only one carbonyl absorption in the infrared (1678 cm.$^{-1}$) and no vinyl hydrogen atom in the n.m.r.


III

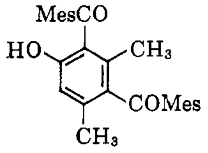

IV


V

Bromination of the mixture of isomers II in the presence of a trace of aluminum chloride gave a monobromo compound (V) of the composition $C_{28}H_{33}BrO_2$. Lack of significant change in the infrared spectrum of V, relative to II, in the carbonyl region suggested that this was not an α-bromo ketone. The n.m.r. spectrum furnishes strong argument for structure V. The triplet vinyl proton resonance of II is replaced by a doublet at 3.44 τ (J = 7 c.p.s.); a new series of four lines has appeared at 5.4 τ (J = 7 c.p.s., J' = 3 c.p.s.) which may be attributed to a lone proton on an allylic carbon atom to which a bromine atom also is attached. This proton is coupled to adjacent vinyl and tertiary alkyl protons. The latter proton which should appear near 8.5 τ[3] is not readily identifiable. Compound V still contains two methyl groups attached to saturated carbon atoms that bear single protons. These spectral changes are consistent only with the transformation of II to V.

Attempts to establish the carbon skeleton of II by dehydrogenation with chloranil or sulfur were unsuccessful. With palladium on charcoal 2,4-dimesitoyltoluene, identified by its characteristic n.m.r. spectrum in the 2–3.5-τ region, was obtained in low yield. It is unlikely that this compound arises by dehydrogenation of a monomethylated dimesitoylbenzene; its isolation, therefore, establishes the position of one of the alicyclic methyl groups in II. The difficulty experienced in dehydrogenating ketone II is attributed to the steric effect of four vicinal substituents on the cyclohexene ring. Demethylation due to crowding has been observed also by Newman, Sagar, and George.[4]

Conversion of both II and V to the same aromatic compound was achieved by means of base-catalyzed autoxidation. The product was assigned structure VI on the basis of its elemental analysis, analysis of its acetate, and spectral evidence. The infrared spectrum showed the presence of a chelated *o*-hydroxy ketone; acetylation effected a shift of the chelated carbonyl group frequency from 1638 to 1672 cm.$^{-1}$. The chemical shift in the n.m.r. of the remaining proton on the central aromatic ring in the phenol and its acetate (3.09 and 2.89 τ) allows tentative assignment of the proton to a position *meta* to the carbonyl groups.


VI

Our expectation that the second methyl group would enter the position adjacent to the mesitoyl groups is consistent with the evidence available; experiments designed to settle the point are in progress.

Experimental[5]

1,3-Dimesitoylbenzene.—To a solution of 50 g. (0.25 mole) of isophthaloyl chloride[6] in 175 ml. of dry methylene chloride was added, with cooling and stirring, 73 g. (0.50 mole) of anhydrous aluminum chloride. A solution of 80 ml. (0.58 mole) of mesitylene and 80 ml. of methylene chloride was added over a period of 2 hr. The mixture was heated at reflux for 1 hr., allowed to cool, and stirred at room temperature for an additional 2 hr. The diketone, isolated by conventional procedures, was recrystallized repeatedly from ethanol–chloroform; yield, 73 g. (92%); m.p. 151–153° (lit.[7] m.p. 149–151°).

Reaction of 1,3-Dimesitoylbenzene with Methylmagnesium Iodide.—To a Grignard reagent made in ethyl ether from 19.1 g. (0.135 mole) of methyl iodide and 3.24 g. (0.135 g.-atom) of magnesium was added in a nitrogen atmosphere a solution of 3.0 g. (8.1 mmoles) of the diketone, 30 ml. of benzene, and 30 ml. of ether. The mixture was heated under reflux for 2 hr. and treated with 80 ml. of 6 *N* hydrochloric acid. The two-phase system was allowed to stand overnight under nitrogen. The product, isolated by usual techniques, was an orange oil (3.7 g.).

On chromatography of this oil over 120 g. of Florisil all of the desired material was eluted with 10:1 cyclohexane–ether. One recrystallization from methanol gave 1.92 g. (59%) of white crystalline solid, m.p. 129–131.5°. A second crop of shorter melting range (125.5–127.5°) was analyzed.

Anal. Calcd. for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.58; H, 8.34.

Crystallization of the crude product from 10 g. of *m*-dimesitoylbenzene from 95% ethanol yielded 6.76 g. of product, m.p. 121–124°. Chromatography of this solid over alkaline alumina (Merck) allowed isolation of 1.5 g. of a higher melting isomer, m.p. 159–160° and 174.5–175.5°, by elution with 12:1 through 8:1 cyclohexane–ether mixtures. Recrystallization from 95% ethanol, methanol, and benzene–hexane afforded an analytical sample, m.p. 159–160° and 174.5–175.5°.

Anal. Calcd. for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.72; H, 8.56.

Infrared spectra of the mixture of isomers and the high melting compound had absorption bands in common at 1690, 1648,

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[2] R. C. Fuson, J. P. Freeman, and J. J. Looker, *J. Org. Chem.*, **26**, 4217 (1961); R. C. Fuson and J. J. Looker, *ibid.*, **27**, 3357 (1962).

[3] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 52.

[4] M. S. Newman, W. C. Sagar, and M. V. George, *J. Am. Chem. Soc.*, **82**, 2376 (1960).

[5] Melting points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 21B spectrometer by Mr. D. H. Johnson, Mr. W. Dalton, Mr. D. Fujii, and Miss D. Wood. N.m.r. spectra were run on a Varian Model A-60 spectrometer with tetramethylsilane as an internal standard. Microanalyses were performed by Mr. Josef Nemeth and associates.

[6] L. Berend and P. Herms, *J. prakt. Chem.*, [2] **74**, 112 (1906).

[7] R. C. Fuson, E. M. Bottorff, R. E. Foster, and S. B. Speck, *J. Am. Chem. Soc.*, **64**, 2573 (1942).

1630, 855, and 845 cm.$^{-1}$, but differed in the number and location of low intensity bands in the region from 1340 to 810 cm.$^{-1}$. Nuclear magnetic resonance spectra of the mixture of isomers and the high melting isomer contained bands assignable to the following structural features: mesityl groups (3.13, 7.72, 7.77, and 7.88 τ), vinyl protons (3.41 τ, triplets, J = 3 c.p.s.), and alicyclic methyl groups (for the mixture of isomers: two doublets, partially superimposed, 8.77 and 8.87 τ; J = 7 and 6 c.p.s.; for the high melting isomer: two doublets, completely superimposed, 8.78 τ, J = 7 c.p.s.).

Ether–absolute ethanol mixtures in the ratios 1:1 and 0:1 also eluted 0.9 g. of the dimethyldimesitoylphenol VI. The analytical sample, recrystallized from ethanol–water and methanol, melted at 206.5–207.5°.

Anal. Calcd. for $C_{28}H_{30}O_3$: C, 81.13; H, 7.30; mol. wt., 414.5. Found: C, 81.05; H, 7.27; mol. wt., 421.

Infrared spectra (Nujol, hexachlorobutadiene, and KBr) indicated the presence of hydroxyl (3320), carbonyl (1658, 1638), and pentasubstituted aromatic (882 cm.$^{-1}$) groups. The n.m.r. spectrum indicated the presence of five aromatic protons in two peaks at 3.10 and 3.15 τ, and only aryl methyl protons at higher field (7.72, 7.82, and 7.93 τ).

Acetylation of the phenol VI by refluxing acetic anhydride afforded an acetate, m.p. 147.5–148.5°, in 86% yield.

Anal. Calcd. for $C_{30}H_{32}O_4$: C, 78.92; H, 7.08. Found: C, 78.94; H, 6.99.

The infrared spectrum ($CHCl_3$) has bands at 1762, 1672–1658 (broad), 883, and 854 cm.$^{-1}$. The n.m.r. spectrum shows one aromatic proton (2.89 τ), four mesityl aromatic protons (3.07 τ), and 27 methyl protons (six peaks, 118–143 c.p.s. downfield from tetramethylsilane).

Reduction of 2,4-Dimesitoyl-3,5-dimethylcyclohexene (II) with Lithium Aluminum Hydride.—To a suspension of 0.4 g. (20 mmoles) of lithium aluminum hydride in 35 ml. of dry ether under an atmosphere of dry nitrogen was added slowly with stirring at room temperature 2.0 g. (5.0 mmoles) of diketone II (mixture of isomers) in 60 ml. of ether. The mixture was stirred at room temperature for 2 hr., then treated with ethyl acetate and 40 ml. of 6 N hydrochloric acid. The ethereal phase was dried over sodium sulfate and concentrated to an oil under reduced pressure. Crystallization from methanol yielded 1.2 g. (60%) of white prisms, m.p. 170–173°. The infrared spectrum showed bands for hydroxyl (3570, 3440), carbonyl (1687), and mesityl (855 cm.$^{-1}$) groups.

Oxidation of 500 mg. of this keto alcohol (III) with chromium trioxide in acetone–sulfuric acid–water[8] yielded 490 mg. (99%) of the diketone IV as small white prisms, m.p. 114–118.5°. Recrystallization from petroleum ether (b.p. 60–70°) afforded an analytical sample, m.p. 118–119°.

Anal. Calcd. for $C_{28}H_{36}O_2$: C, 83.12; H, 8.97. Found: C, 83.15; H, 8.92.

The infrared spectrum ($CHCl_3$) has significant bands at 1678, 1670 (shoulder), and 853 cm.$^{-1}$; no hydroxyl absorption is present. The n.m.r. spectrum indicates loss of the vinyl proton. Resonance lines at 3.20, 7.68, 7.73, and 7.76 τ; 8.88 and 9.14 τ (two doublets, J = 6.5 c.p.s.); and in the regions 80–130 and 160–225 c.p.s. below tetramethylsilane indicate the presence of mesityl groups and two methyl groups, attached to carbon atoms bearing lone hydrogen atoms, on a cyclohexane ring.

Bromination of 2,4-Dimesitoyl-3,5-dimethylcyclohexene.—A solution of 1.0 g. (2.49 mmoles) of ketone II (mixture of isomers) in 20 ml. of dry ether was treated in an ice bath with a trace of anhydrous aluminum chloride, then dropwise with 0.125 ml. (2.49 mmoles) of bromine in 5 ml. of ether. After 15 min. the mixture was poured onto ice and the ether layer was decanted through anhydrous sodium sulfate. The ether was removed with as little heating as possible. Crystallization of the residual oil from petroleum ether furnished 640 mg. (54%) of white crystals, m.p. 146–148°. One further recrystallization furnished an analytical sample, m.p. 147–148°.

Anal. Calcd. for $C_{28}H_{33}BrO_2$: C, 69.84; H, 6.91. Found: C, 69.81; H, 6.85.

The infrared spectrum ($CHCl_3$) shows absorption at 1688 (shoulder), 1676, 1658, 1640 (shoulder), and 850 cm.$^{-1}$. The n.m.r. spectrum shows resonance lines at the following positions: 3.44 τ (doublet, J = 7 c.p.s.), 5.40 τ (doublet, further split, J = 7 c.p.s., J' = 3 c.p.s.), 8.79 and 9.03 τ (two doublets, J = 6.5 c.p.s.).

Treatment of Bromo Ketone V with Base and Air.—A suspension of 200 mg. of the bromo ketone V in 10 ml. of absolute ethanol was treated with 1.0 g. of potassium hydroxide dissolved in 20 ml. of ethanol. The mixture was stirred at room temperature for 4 hr. with exposure to air. The solution was acidified with dilute hydrochloric acid, filtered free from precipitated salts, and the ethanol removed by distillation. The residue was extracted with ether and the ethereal solution washed with water and dried. After removal of the solvent, the residue crystallized from hexane to give 100 mg. of a white compound, m.p. 205.5–207.5°. This compound was shown by melting point, mixture melting point, and identity of infrared spectra to be 2,4-dimesitoyl-3,5-dimethylphenol (VI), isolated previously from chromatography of the diadduct II over alkaline alumina.

Treatment of 2,4-Dimesitoyl-3,5-dimethylcyclohexene (II) with Base and Air.—The diketone II (mixture of isomers) (3.1 g., 7.7 mmoles), 50 ml. of dimethyl sulfoxide, and 0.83 g. (15.4 mmoles) of anhydrous sodium methoxide were mixed and stirred under exposure to air (with exclusion of moisture) for 20 hr. at room temperature. The mixture was acidified, diluted with an equal volume of water, and extracted with ether. The ethereal solution was washed with 10% sodium carbonate solution, dilute hydrochloric acid, and water, and dried. Removal of the solvent under reduced pressure provided an oil which crystallized from methanol-water to give 1.41 g. of solid, m.p. 200.5–204.5°. One recrystallization from methanol raised the melting point to 205.5–206.5°; the melting point was not depressed on admixture with a sample of the phenol VI isolated from the alumina chromatography of ketone II. If the reaction was carried out as before but under a nitrogen atmosphere for 18 hr., the starting ketone II was recovered in nearly quantitative yield, m.p. 129–131°.

Attempted Dehydrogenation of 2,4-Dimesitoyl-3,5-dimethylcyclohexene (II).—The diketone II (830 mg., mixture of isomers) was mixed with 100 mg. of 10% palladium on charcoal and heated at 300° under a nitrogen atmosphere for 1.5 hr. The mixture was freed from catalyst and the products were chromatographed over 80 g. of Merck alumina. With cyclohexane–ether in the ratios 8:1 through 5:1 there was eluted an oil which could be crystallized from acetone–water; m.p. 148–148.5°. Attempted sublimation seemed to effect decomposition. However, the residue from sublimation was recrystallized several times from petroleum ether to give 30 mg. of a compound melting at 153–155°. The infrared spectrum has bands at 1667, 856, and 814 cm.$^{-1}$, which are in accord with the structure 2,4-dimesitoyltoluene. The n.m.r. spectrum shows two doublets of an AB spin system (2.27, 2.68 τ, J = 7.5 c.p.s., J' = 2.5 c.p.s.), the lower of which is further split by coupling with another aromatic proton (2.43 τ, J' = 2.5 c.p.s.), one methyl group on the central aromatic ring (7.30 τ), and the expected lines for mesityl aromatic and methyl protons (3.26 and 7.72, 8.03 and 8.08 τ).

The n.m.r. spectrum of 2,4-dinitrotoluene shows a closely analogous pattern in the aromatic region, but the peaks are all shifted to lower field: 1.22 τ (doublet, J' = 2 c.p.s.); 1.62 τ (doublet, further split, J = 9 c.p.s., J' = 2 c.p.s.); and 2.29 τ (doublet, J = 9 c.p.s.). The latter two doublets are assigned to the vicinal aromatic protons.[9]

Reaction of 1,3-Dimesitoylbenzene with Benzylmagnesium Chloride.—To a solution of the Grignard reagent prepared in ethyl ether from 59 ml. (0.514 mole) of benzyl chloride and 12.3 g. (0.514 g.-atom) of magnesium was added as rapidly as possible a solution of 19.0 g. (0.0527 mole) of the diketone, 60 ml. of benzene, and 60 ml. of ether. The mixture was heated at reflux for 2 hr. and treated with 200 ml. of 6 N hydrochloric acid; the two-phase mixture was allowed to stand overnight. The product was recrystallized from 95% ethanol, m.p. 156–159°, yield 13 g. (44.4%). Recrystallization of the compound from ethanol–chloroform raised the melting point to 173.5–174.5°.

Anal. Calcd. for $C_{40}H_{42}O_2$: C, 86.60; H, 7.63; mol. wt., 554.7. Found: C, 86.56; H, 7.63; mol. wt., 558.

The infrared spectrum ($CHCl_3$) shows absorption at 1687, 1634, and 860 cm.$^{-1}$. A second spectrum (Nujol) indicates the presence of monosubstituted phenyl groups (731 and 702 cm.$^{-1}$). The ultraviolet spectrum (1.86 × 10^{-5} M in absolute ethanol)

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(8) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(9) See, for example, N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, spectra number 149, 233, and 293.

also supports structure 2,4-dimesitoyl-3,5-dibenzylcyclohexene; it has a shoulder at 242 mμ (ε 16,200).

Reduction of 2,4-Dimesitoyl-3,5-dibenzylcyclohexene with Lithium Aluminum Hydride.—A solution of 4 g. (0.0043 mole) of the diketone in 50 ml. of dry tetrahydrofuran was added slowly with stirring to a suspension of 0.42 g. (0.013 mole) of lithium aluminum hydride in 50 ml. of dry tetrahydrofuran. The reaction mixture was stirred at room temperature for 1.5 hr., and the excess hydride decomposed by cautious addition of ice chips with the flask immersed in an ice bath. The product, isolated by conventional procedures, was recrystallized from ethanol–chloroform; m.p. 193–193.7°; yield, 2.15 g. (53.4%). Further recrystallization from ethanol gave long white needles melting at 200–200.5°.

Anal. Calcd. for $C_{40}H_{46}O_2$: C, 85.97; H, 8.30. Found: C, 85.62; H, 8.41.

The infrared spectrum (Nujol, hexachlorobutadiene) has bands at 3460, 1680 (broad), and 857 cm.$^{-1}$, which are to be expected for 3-mesitoyl-2,6-dibenzylcyclohexylmesitylcarbinol.

Acetylation of 0.2 g. of the carbinol gave the acetate, which crystallized from ethanol; m.p. 135–136°; yield, 59%. The infrared spectrum (Nujol, hexachlorobutadiene) has bands for acetate (1730), ketone (1694), and mesityl (855 cm.$^{-1}$) groups.

Oxidation of the carbinol with chromium trioxide in pyridine[10] gave 2,4-dibenzyl-1,3-dimesitoylcyclohexane, which crystallized from ethanol–chloroform as white prisms, m.p. 152.5–154°. The infrared spectrum (Nujol, hexachlorobutadiene) is consistent with the structure 2,4-dibenzyl-1,3-dimesitoylcyclohexane (ν_{max} 1689, 1680, 857 cm.$^{-1}$; no band is found in the O–H stretching region).

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[10] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarrett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

2,4-Dinitrophenylhydrazones. IV.[1] The Reactions of Vinyl Ketones and β-Alkoxy Ketones. The Formation of Substituted 6-Nitrobenzotriazole Oxides

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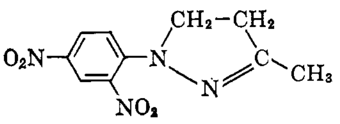
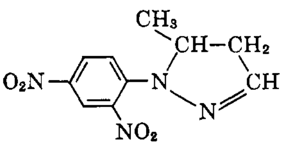
The compound described by Matsoyan and Vartanyan as 3-methyl-1-(2,4-dinitrophenyl)pyrazoline has been prepared in several ways. The ethyl analog also has been prepared. These compounds are shown not to be the pyrazolines. It is proposed that they are 3-(3′-oxobutyl)-6-nitrobenzotriazole 1-oxide and 3-(3′-oxopentyl)-6-nitrobenzotriazole 1-oxide, respectively. The 2,4-dinitrophenylhydrazones of four 4-alkoxybutanones have been made. It is shown that the derivatives recorded by Matsoyan and Vartanyan are not the 2,4-dinitrophenylhydrazones. Data in the literature concerning ethyl vinyl ketone 2,4-dinitrophenylhydrazone and 3-ethyl-1-(2,4-dinitrophenyl)pyrazoline are corrected.

Some years ago one of us showed[1] that the newly reported[2] technique for preparing 2,4-dinitrophenylhydrazones could be used with acid-sensitive carbonyl compounds and gave as an illustration the preparation of the derivative of methyl vinyl ketone. Although this ketone has been known for many years its 2,4-dinitrophenylhydrazone had not, as we thought, been reported. Actually, we found later that Martin had reported the derivative also in 1959.[3] We had pointed out[2] that unless care were exercised in preparing the derivative of this ketone one might obtain instead, for example, the derivative of a 4-alkoxybutanone. We also had noted Nazarov's[4] report that treatment of methyl vinyl ketone with 2,4-dinitrophenylhydrazine in acidic ethanol–dioxane solution gave a solid with a melting point of 217° and a carbon analysis 2.3% low for the expected derivative.

We were interested in Nazarov's compound and our interest led us in the direction of the derivatives of 4-alkoxybutanones and the formation of pyrazolines. As a result we found some conflicting observations in the literature, the attempted clarification of which has resulted in the present work.

In a paper by Matsoyan[5] on 4-alkoxybutanones and pyrazolines, two observations aroused our interest. The first was that by boiling a mixture of 4-alkoxybutanones in strongly acidic, ethanolic 2,4-dinitrophenylhydrazine a compound was obtained having a melting point of 160–161°, and this was described as 3-methyl-1-(2,4-dinitrophenyl)pyrazoline (I). Now it happened that we had had occasion earlier to prepare this pyrazoline and its 5-methyl isomer (II). Our melting points were close to those already reported by Mousseron[6]; namely, 131–132° for the 3-methyl (lit.[6] 129–130°) and 117.5–119° for the 5-methyl (lit.[6] 114–115°) isomer.


I


II

The second was in the list of 2,4-dinitrophenylhydrazones of twelve 4-alkoxybutanones.[5] When we examined this list we were struck by the fact that six of the derivatives had melting points covered by the range 211 to 221°. An identical list of derivatives, except for the omission of the last two, is given by Nazarov.[7] The coincidence in melting points of the six derivatives with that of Nazarov's[4] unknown compound was obvious.

Thus, it appeared that Matsoyan's pyrazoline was not I or II and that some interesting chemistry linked methyl vinyl ketone and the 4-alkoxybutanone deriva-

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[1] (a) For paper III see H. J. Shine, *J. Org. Chem.*, **24**, 1790 (1959); (b) taken in part from the M.S. thesis of Li-Tzu Fang, Texas Technological College, August, 1962; (c) the financial support for this work was obtained in the form of a grant (no. 1603AD) from Texas Technological College, for which we express our gratitude.

[2] H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959).

[3] G. Martin, *Ann. chim.*, **13** (4), 541 (1959).

[4] I. N. Nazarov, L. A. Kasitsyna, and I. I. Zaretskaya, *Zh. Obshch. Khim.*, **27**, 606 (1957).

[5] S. G. Matsoyan and S. A. Vartanyan, *Izv. Akad. Nauk Arm. SSR, Ser. Fiz. Mat., Estestven. Tekh. Nauk.*, **8**, 31 (1955).

[6] M. Mousseron, R. Jacquier, and J. Brun, *Compt. rend.*, **247**, 617 (1958).

[7] I. N. Nazarov, S. A. Vartanyan, S. G. Matsoyan, and V. N. Zhamagortsyan, *Zh. Obshch. Khim.*, **23**, 1986 (1953).