The Synthesis and Some Reaction of 3-Acetonyltropolones

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In a previous paper,[1] it was described how 3-acetyl-8-hydroxy-1-oxaazulan-2-one (3-acetyl-8-hydroxy-2*H*-cyclohepta[b]furan-2-one) (I) was obtained by the condensation reaction of 3-bromotropolone and ethyl acetoacetate. By the extension of this reaction to alkyl derivatives of 3-bromotropolone, the alkyl derivatives of I were also synthesized.[1] During the studies of the examination of their chemical behavior, it has been found that the alkaline hydrolysis of I affords 3-acetonyltropolone (II). Since the tropolone derivatives with a carbonyl function in their side-chain are very interesting in the synthetical studies of troponoid, the synthesis and some reactions of 3-acetonyltropolones have now been examined.

When 3-acetyl-8-hydroxy-1-oxaazulan-2-one (I) was heated in hydrobromic acid, it was converted into 3-carboxymethyltropolone (III), as has been reported.[1] However, when heated

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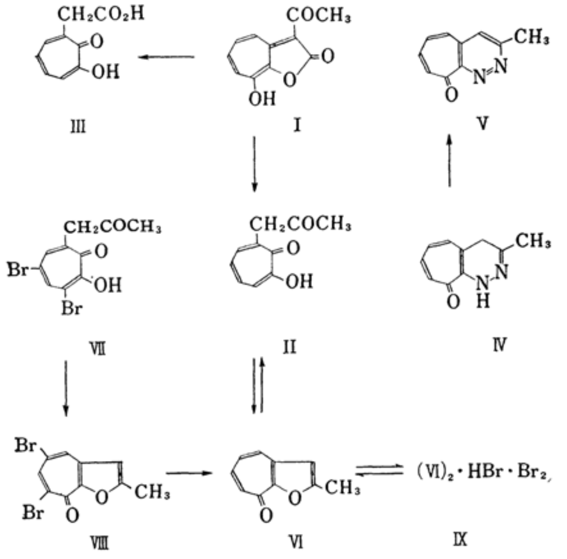
[1] K. Takase, This Bulletin, 37, 1460 (1964).

in a potassium hydroxide or sodium hydroxide solution, the compound I gave a ketonic compound II, from which an oxime, a semicarbazone, a phenylhydrazone and a 2,4-dinitrophenylhydrazone were derived. The tropolonic nature of II was shown from the facts that it was soluble in alkali, showed a positive ferric chloride coloration, and gave a green copper chelate. Its ultraviolet absorption spectrum, which is similar to that of 3-methyltropolone,1) also supports its tropolonic structure. From these evidences and its elemental analysis, II is assumed to be 3-acetonyltropolone, produced by the hydrolysis of the lactone ring of I, followed by decarboxylation. It is interesting that, when heated with a sodium methoxide solution, I did not hydrolize into II, but was converted into 3-carboxymethyltropolone (III). It is known that the treatment of acetoacetic esters with dilute alkali gives ketones by ketonic hydrolysis, but with sodium alcoholate, esters are obtained by acidic hydrolysis.2) In the case of I, it was found that a similar cleavage was also caused by sodium methoxide.

Although II produced the normal carbonyl derivatives in the reaction with the usual carbonyl reagents, as has been mentioned above, when heated with hydrazine it gave a bicyclic compound: 1,4-dihydro-3-methylpyridazo[3,4-b]tropone (IV). Its structure was deduced on the basis of the facts that it was insoluble in alkali and showed a negative ferric chloride coloration. Its ultraviolet absorption spectrum is similar to those of alkylidene derivatives of 2-hydrazinotropones,3) as is shown in Fig. 1, and its infrared spectrum shows the absorption of an N–H stretching vibration of secondary amine at 3270 cm^{-1}. The compound IV was dehydrogenated by treatment with nitric acid, affording 3-methylpyridazo[3,4-b]tropone (V), whose ultraviolet absorption spectrum is shown in Fig. 1.

When heated in concentrated sulfuric acid or hydrochloric acid, II gave a basic compound VI, which in turn produced a picrate and a styphnate. This compound did not show the tropolonic enolone or the carbonyl nature;



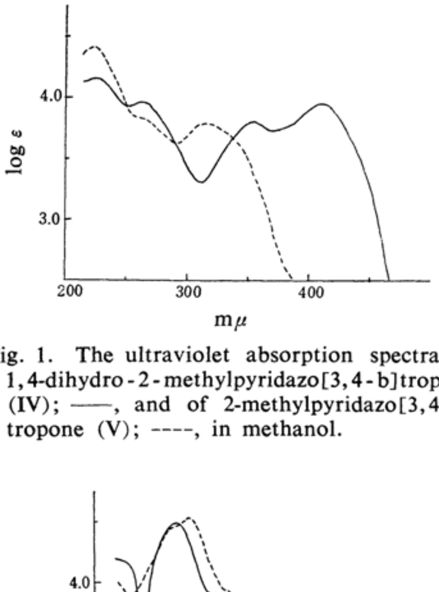


Fig. 1. The ultraviolet absorption spectra of 1,4-dihydro-2-methylpyridazo[3,4-b]tropone (IV); ——, and of 2-methylpyridazo[3,4-b]-tropone (V); ----, in methanol.

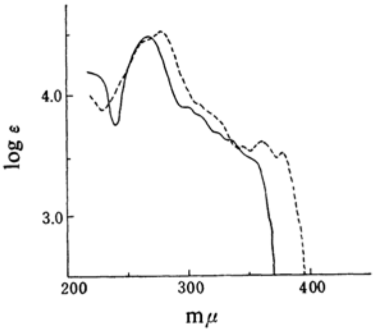
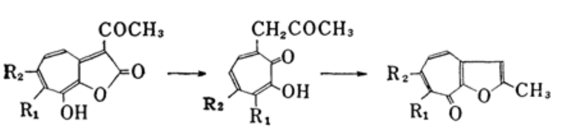


Fig. 2. The ultraviolet absorption spectra of 2-methylfuro[2,3-b]tropone (VI); ——, and of 5,7-dibromo-2-methylfuro[2,3-b]tropone (VIII); ----, in methanol.



Xa: $R_1=CH_3$, $R_2=H$
Xb: $R_1=H$, $R_2=i\text{-}C_3H_7$

XIa: $R_1=CH_3$, $R_2=H$
XIb: $R_1=H$, $R_2=i\text{-}C_3H_7$

XIIa: $R_1=CH_3$, $R_2=H$
XIIb: $R_1=H$, $R_2=i\text{-}C_3H_7$

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2) C. R. Hauser and B. E. Hudson, Jr., "Organic Reactions," Vol. 1, pp. 266-302.

3) K. Takase, This Bulletin, 37, 1288 (1964); T. Nozoe and J. Shin, to be published.

it was insoluble in alkali, showed a negative ferric chloride coloration, and did not give any carbonyl derivative. In its infrared spectrum in KBr, no absorption appears in the region of the stretching vibration of the tropolonic hydroxyl or of the carbonyl of the acetonyl group. However, when VI was heated in a dilute alkali solution, the tropolone (II) was reproduced. These facts show that VI has the same carbon-skeleton as II, but the tropolonic hydroxyl group and the carbonyl group in the side-chain are masked. From these evidences and its elemental analysis, VI is assumed to be 2-methylfuro [2, 3-b] tropone produced from II by ring formation under dehydration. Its ultraviolet absorption spectrum, as is shown in Fig. 2, is considerably different from those of tropones or tropolones in the long wave region (300—400 mμ). This fact shows that VI belongs to a new aromatic ring system.

The behavior of II in relation to some cationoid reagents, such as aryldiazonium salt or bromine, was also examined. When treated with a *p*-toluenediazonium chloride solution, II gave an azo compound, in which the position of the azo group is assumed to be at the 5-position, in analogy to the other azotropolone.[4]

The bromination of II in methanol, in the presence of sodium acetate, afforded a dibromo compound VII, which is assumed to be 5, 7-dibromo-3-acetonyltropolone since it is soluble in alkali, shows a positive ferric chloride coloration, and gives a 2, 4-dinitrophenylhydrazone. The positions of the bromines were inferred from the following evidence. It was expected that the compound which brominated in the acetonyl side-chain would be unstable to alkali, but this compound was stable. On the other hand, it is well-known that the bromination of the tropolone nucleus is easily attained at the 3, 5 or 7-position.[4] When the bromination of II was undertaken in methanol without the presence of sodium acetate, VII could not be obtained, but a dibromo compound VIII was produced, accompanied with the formation of VI. The dibromo compound VIII was also obtained when VII was heated with concentrated sulfuric acid. The ultraviolet absorption spectrum of VIII is similar to that of VI, as is shown in Fig. 2. The reductive debromination of VIII afforded VI. From these facts, VIII is assumed to be 5, 7-dibromo-2-methylfuro [2, 3-b] tropone. Since VI did not gave any brominated compound under these conditions, the formation of VIII from II is considered to proceed through VII, which is produced by the bromination of II and which then forms the furan ring by the action of hydrogen bromide in a way similar to that of II.

The furo [2, 3-b] tropone (VI) changed to 3-acetonyltropolone (II) by alkali, as has been mentioned before, but it was very stable to acid. It resists the action of the cationoid reagents, such as nitric acid, nitrous acid or aryldiazonium salts. The bromination of VI in acetic acid did not give the brominated compound, but it produced a complex compound IX, which easily reproduced VI when treated with a sodium hydrogen sulfite solution. Similar complex compounds of tropone[5] or tropolone[6] and bromine have been known, but IX is more stable than the corresponding tropone- or tropolone-complex; the former could not be converted into an addition or substitution product, while the latter could. When treated with *N*-bromosuccinimide, VI gave a monobromo compound, which is considered from its ultraviolet absorption curves to be a bromo-substituted derivative of VI but the position of the substitution is not yet clear.

The alkyl derivatives of I, 3-acetyl-7-methyl-8-hydroxy-1-oxaazulan-2-one (Xa) and 3-acetyl-6-isopropyl-8-hydroxy-1-oxaazulan-2-one (Xb)[1] also gave 3-acetonyltropolone derivatives (XIa and XIb) by alkaline hydrolysis. These compounds showed a positive ferric chloride coloration and reacted with carbonyl reagents in a manner similar to II. When they were treated with concentrated sulfuric acid, furo[2, 3-b]-tropone derivatives (XIIa and XIIb) were obtained. The chemical behaviors of these compounds were similar to those of VI; they were insoluble in alkali and gave a picrate and a styphnate respectively. Their ultraviolet absorption curves are also similar to that of VI.

Experimental[7]

3-Acetonyltropolone (VI). — A solution of I (1.00 g.) in a 2 N potassium hydroxide solution (10 ml.) was heated under reflux for 3 hr., and then the mixture was acidified with 6 N hydrochloric acid and extracted with chloroform. The solvent was evaporated and the residue was recrystallized from cyclohexane to give II (550 mg.) as colorless needles, m. p. 86—87°C.

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[4] Cf. T. Nozoe, *Fortschr. Chem. organ. Naturstoffe*, **13**, 233 (1956); T. Nozoe et al., "Dai Yuki Kagaku" ("Comprehensive Organic Chemistry"), Vol. 13, Chapters 5, 6, 8 and 9, Asakura Shoten, Tokyo (1960).

[5] T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ.*, **I**, **39**, 164 (1956).

[6] T. Nozoe, S. Seto, T. Mukai, K. Yamane and A. Matsukuma, *Proc. Japan Acad.*, **27**, 224 (1951).

[7] All melting points are uncorrected.

Found: C, 67.09; H, 6.09. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%. λ_{max}^{MeOH} mμ (log ε): 240 (4.27), 330 (3.95), 392 (3.92).

The same treatment of I (200 mg.) with a 2 N sodium hydroxide solution (2.5 ml.) also afforded II (90 mg.).

Copper Chelate: m. p. 253°C, green crystals.

Oxime: m. p. 127—128°C, colorless prisms (from ethanol).

Found: C, 61.88; H, 5.70; N, 7.28. Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25%.

Semicarbazone: m. p. 189—189.5°C, colorless silky needles (from ethanol).

Found: C, 56.37; H, 5.59; N, 18.00. Calcd. for $C_{11}H_{13}O_3N_3$: C, 56.16; H, 5.57; N, 17.86%.

Phenylhydrazone: m. p. 138 — 138.5°C, yellow needles (from benzene).

Found: C, 71.88; H, 5.88; N, 10.59. Calcd. for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

2, 4-Dinitrophenylhydrazone: m. p. 170.5—171°C, reddish orange needles (from ethanol).

Found: C, 53.37; H, 4.18; N, 15.77. Calcd. for $C_{16}H_{14}O_6N_4$: C, 53.63; H, 3.94; N, 15.64%.

The Reaction of I with Sodium Methoxide.—To a sodium methoxide solution prepared from sodium (100 mg.) and methanol (4 ml.), I (200 mg.) was added, and the mixture was heated under reflux for 6 hr. The solvent was then evaporated, and the residue was dissolved in water and acidified with 6 N hydrochloric acid. Continuous extraction with ether for 8 hr. afforded 3-carboxymethyltropolone (III) (120 mg.), m. p. 171°C (decomp.).

1, 4-Dihydro-3-methylpyridazo[3,4-b]tropone (IV).—When mixture of II (200 mg.), 80% hydrazine hydrate (150 mg.) and ethanol (1 ml.) was allowed to stand for 2 hr. at room temperature, yellow hydrazine salt (150 mg., m. p. 119°C), was separated out.

Found: C, 54.20; H, 6.60; N, 23.14. Calcd. for $C_{10}H_{16}O_2N_4$: C, 53.55; H, 7.19; N, 24.98%.

This mixture was heated under reflux for 30 min. and then allowed to cool; the crystals thereby obtained were recrystallized from ethanol to give IV (100 mg.) as yellow plates, m. p. 145—146°C.

Found: C, 68.67; H, 5.49; N, 15.98. Calcd. for $C_{10}H_{10}ON_2$: C, 68.95; H, 5.79; N, 16.08%. λ_{max}^{MeOH} mμ (log ε): 225 (4.16), 265 (3.94), 350 (3.78), 414 (3.98).

3-Methylpyridazo[3, 4-b]tropone (V).—A mixture of IV (90 mg.) and concentrated nitric acid (0.5 ml.) was stirred at room temperature. After the evolution of gas had ceased, the mixture was neutralized with a 2 N potassium hydroxide solution and extracted with chloroform. The crystals obtained after the removal of the solvent were recrystallized from benzene to give V (20 mg.) as pale yellow prisms, m. p. 189°C (decomp.).

Found: C, 69.72; H, 5.01; N, 16.08. Calcd. for $C_{10}H_8ON_2$: C, 69.79; H, 4.68; N, 16.27%. λ_{max}^{MeOH} mμ (log ε): 225 (4.40), 315 (3.77).

2-Methylfuro[2, 3-b]tropone (VI).—After a mixture of II (200 mg.) and concentrated sulfuric acid (0.5 ml.) had been heated at 100°C for 5 min., it was diluted with water (3 ml.) and extracted with chloroform. The removal of the solvent gave an oily substance, which was solidified by cooling. Sublimation under reduced pressure and recrystallization from a mixture of benzene and petroleum ether gave VI (180 mg.) as colorless needles, m. p. 49—50.5°C.

Found: C, 70.99; H, 5.24; H_2O, 5.18. Calcd. for $C_{10}H_8O_2\cdot1/2H_2O$: C, 70.99; H, 5.36; H_2O, 5.32%. λ_{max}^{MeOH} mμ (log ε): 251 (4.48), 300 (3.90), 335 (3.62).

The same result was obtained with concentrated hydrochloric acid in place of sulfuric acid.

Picrate: m. p. 142—143°C, yellow needles (from ethanol).

Found: C, 49.31; H, 3.05; N, 11.25. Calcd. for $C_{10}H_8O_2\cdot C_6H_3O_7N_3$: C, 49.36; H, 2.85; N, 10.80%.

Styphnate: m. p. 164 — 165°C, yellow prisms (from ethanol).

Found: C, 47.39; H, 2.87; N, 9.94. Calcd. for $C_{10}H_8O_2\cdot C_6H_3O_8N_3$: C, 47.42; H, 2.74; N, 10.37%.

The Reaction of VI with Alkali.—A mixture of VI (100 mg.) and 2 N potassium hydroxide solution (1.5 ml.) was heated under reflux for 2 hr., it was then acidified with 6 N hydrochloric acid and extracted with chloroform. The solvent was evaporated and residue was recrystallized from cyclohexane to give II (50 mg.), m. p. 86—87°C.

5-(*p*-Tolylazo)-3-acetonyltropolone.—To a stirred solution of II (100 mg.) in pyridine (3 ml.), a solution of *p*-toluenediazonium chloride, prepared from *p*-toluidine (70 mg.) in the usual manner, was added, and the mixture was stirred for 1 hr. Water was added, and the crystals obtained were recrystallized from cyclohexane to give the azo compound (160 mg.) as reddish-orange prisms, m. p. 133—134°C.

Found: C, 69.29; H, 5.43; N, 9.84. Calcd. for $C_{17}H_{16}O_3N_2$: C, 68.90; H, 5.44; N, 9.45%. λ_{max}^{MeOH} mμ (log ε): 232 (4.31), 290 (4.08), 400 (4.43), 435 (4.41).

5, 7-Dibromo-3-acetonyltropolone (VII). — To a suspension of II (90 mg.) and sodium acetate (100 mg.) in methanol (2 ml.), bromine (160 mg.) was added, and the mixture was stirred for 3 hr. under cooling. Water was added, and the crystals thereby obtained were recrystallized from methanol to give VII (120 mg.) as pale yellow needles, m. p. 155—156°C.

Found: C, 35.75; H, 2.54. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.74; H, 2.40%. λ_{max}^{MeOH} mμ (log ε): 262 (4.43), 347 (4.10), 428 (3.85).

2, 4 - Dinitrophenylhydrazone: m. p. 198 — 199°C, orange scales (from ethanol).

Found: C, 37.55; H, 2.51; N, 10.54. Calcd. for $C_{16}H_{12}O_6N_4Br_2$: C, 37.22; H, 2.34; N, 10.85%.

5, 7-Dibromo-2-methylfuro[2, 3-b]tropone (VIII). —*a) By the Heating of VII with Sulfuric Acid.*—A mixture of VII (100 mg.) and concentrated sulfuric acid (0.3 ml.) was heated at about 100°C for 5 min. and diluted with water to give VIII (70 mg.). Recrystallization from ethanol afforded colorless needles, m. p. 209°C (decomp.).

Found: C, 37.72; H, 2.05. Calcd. for $C_{10}H_6O_2\cdot Br_2$: C, 37.65; H, 1.09%. λ_{max}^{MeOH} mμ (log ε): 278 (4.52), 362 (3.61), 378 (3.51).

b) By the Bromination of II.—To a solution of

II (100 mg.) in methanol (1.5 ml.), bromine (200 mg.) was added, and the mixture was stirred for 1 hr. under cooling. When the solvent was removed and the residue was recrystallized from ethanol, VIII (50 mg.) was obtained as colorless needles, m. p. 209°C (decomp.).

From the mother liquor, an oily substance (40 mg.) was obtained by extraction with chloroform. This oil gave a picrate, m. p. 143°C, undepressed by admixture with the picrate of VI.

The Debromination of VIII.—A solution of VIII (120 mg.) and sodium acetate (100 mg.) in methanol (4 ml.) was shaken with hydrogen in the presence of 5% palladium on carbon; 19.4 ml. (at 20°C) of hydrogen was absorbed during 5 hr. After had been filtered off the catalyst, the evaporation of the solvent left an oily substance (50 mg.), which gave a picrate, m. p. 143°C, undepressed by admixture with the picrate of VI.

The Reaction of VI with Bromine.—To a solution of VI (160 mg.) in glacial acetic acid (1 ml.), bromine (170 mg.) was added, and the mixture was stirred for 1 hr. under cooling. The complex compound (IX) (200 mg.) was obtained as orange needles, m. p. 135—136°C.

Found: C, 43.00; H, 3.29. Calcd. for $(C_{10}H_8O_2)_2\cdot HBr_3$: C, 42.81; H, 3.05%.

This compound (100 mg.) was shaken with a sodium hydrogen sulfite solution and extracted with chloroform to give an oily substance (60 mg.), which gave a picrate, m. p. 143°C, undepressed by admixture with the picrate of VI.

The Reaction of VI and *N*-Bromosuccinimide.—A solution of VI (500 mg.), *N*-bromosuccinimide (570 mg.) and benzoyl peroxide (10 mg.) in carbon tetrachloride (15 ml.) was heated under reflux for 2 hr. The solvent was then evaporated, and the residue was extracted with chloroform. The evaporation of the solvent left an oily substance containing some crystals. The addition of methanol gave crystals (260 mg.), m. p. 145—150°C, which were recrystallized from methanol to give bromo-2-methylfuro[2, 3-b]tropone as colorless needles, m. p. 169—170°C.

Found: C, 50.57; H, 3.02. Calcd. for $C_{10}H_7O_2Br$: C, 50.24; H, 2.95%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 220 (4.17), 278 (4.32).

3-Acetonyl-7-methyltropolone (XIa).—A solution of 3-acetyl-7-methyl-8-hydroxy-1-oxaazulan-2-one (Xa) (100 mg.) in a 2 N potassium hydroxide solution (2 ml.) was heated under reflux for 3 hr. The mixture was then acidified with 6 N hydrochloric acid and extracted with chloroform. The evaporation of the solvent and the recrystallization of the residue from cyclohexane gave XIa (60 mg.) as colorless needles, m. p. 106—107°C.

Found: C, 68.90; H, 6.50. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 245 (4.45), 323 (3.82), 355 (3.77), 370 (3.77).

2, 4-Dinitrophenylhydrazone: m. p. 173 — 174°C, orange needles (from ethanol).

Found: C, 55.22; H, 4.43; N, 14.89. Calcd. for $C_{17}H_{16}O_6N_4$: C, 54.84; H, 4.33; N, 15.05%.

3-Acetonyl-6-isopropyltropolone (XIb).—A solution of 3-acetyl-6-isopropyl-8-hydroxy-1-oxaazulan-2-one (Xb) (1.00 g.) in a 2 N potassium hydroxide solution (20 ml.) was treated in a manner similar to that used in the above experiment. Recrystallization from methanol gave XIb (590 mg.) as colorless needles, m. p. 101—102°C.

Found: C, 70.73; H, 7.29. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 245 (4.47), 328 (3.91), 355 (3.86), 370 (3.84).

Oxime: m. p. 125—126°C, colerless scales (from methanol).

Found: C, 66.43; H, 6.95; N, 5.83. Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28; N, 5.95%.

Semicarbazone: m. p. 129—130°C, colorless microneedles (from ethanol).

Found: C, 60.35; H, 6.77; N, 15.31. Calcd. for $C_{14}H_{19}O_3N_3$: C, 60.63; H, 6.91; N, 15.15%.

Phenylhydrazone: m. p. 110—111°C, yellow needles (from ethanol).

Found: C, 73.41; H, 6.95; N, 9.15. Calcd. for $C_{19}H_{22}O_2N_2$: C, 73.52; H, 7.14; N, 9.03%.

2, 4-Dinitrophenylhydrazone: m. p. 162 — 163°C, orange microneedles (from ethanol).

Found: C, 56.91; H, 4.88; N, 14.18. Calcd. for $C_{19}H_{20}O_6N_4$: C, 56.99; H, 5.04; N, 13.99%.

5-(*p*-Tolylazo)-3-acetonyl-6-isopropyltropolone.—To a stirred solution of XIb (200 mg.) in pyridine (5 ml.), a solution of a *p*-toluenediazonium chloride solution, prepared from *p*-toluidine (100 mg.) in the usual manner, was added under cooling, and the mixture was stirred for 2 hr. Water was added, and the crystals obtained were recrystallized from benzene to give the azo compound (250 mg.) as reddish silky needles, m. p. 154—155°C.

Found: C, 70.72; H, 6.58; N, 8.28. Calcd. for $C_{20}H_{22}O_3N_2$: C, 70.98; H, 6.55; N, 8.28%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 235 (4.29), 295 (4.05), 390 (4.35).

2, 7-Dimethylfuro[2, 3-b]tropone (XIIa).—A mixture of XIa (100 mg.) and concentrated sulfuric acid (1 ml.) was heated at about 100°C for 5 min., then diluted with water and extracted with chloroform. The evaporation of the solvent and the recrystallization of the residue from cyclohexane gave XIIa (80 mg.) as colorless prisms, m. p. 62—64°C.

Found: C, 76.07; H, 5.51. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 225 (4.12), 268 (4.44), 337 (3.61), 352 (3.49).

Picrate: m. p. 110°C, yellow needles (from ethanol).

Found: C, 50.82; H, 3.10; N, 10.66. Calcd. for $C_{11}H_{10}O_2\cdot C_6H_3O_7N_3$: C, 50.63; H, 3.25; N, 10.42%.

Styphnate: m. p. 100 — 101°C, yellow needles (from ethanol).

Found: C, 48.84; H, 3.10; N, 10.24. Calcd. for $C_{11}H_{10}O_2\cdot C_6H_3O_8N_3$: C, 48.69; H, 3.13; N, 10.02%.

6-Isopropyl-2-methylfuro[2, 3-b]tropone (XIIb).—A mixture of XIb (200 mg.) and concentrated sulfuric acid (0.5 ml.) was treated in a manner similar to that used in the above experiment, and the product was distilled under reduced pressure to give XIIb (180 mg.) as a pale yellow oil.

Found: C, 74.00; H, 6.98. Calcd. for $C_{13}H_{14}O_2\cdot 1/2H_2O$: C, 73.91; H, 7.16%. $\lambda_{max}^{\text{MeOH}}$ mμ (log ε): 230 (4.23), 270 (4.39).

Picrate: m. p. 158—159°C, yellow scales (from ethanol).

Found: C, 52.64; H, 3.69; N, 9.90. Calcd. for

$C_{13}H_{14}O_2 \cdot C_6H_3O_7N_3$: C, 52.90; H, 3.97; N, 9.74%.

Styphnate: m. p. 150 — 151°C, yellow needles (from ethanol).

Found: C, 51.06; H, 3.99; N, 9.25. Calcd. for $C_{13}H_{14}O_2 \cdot C_6H_3O_8N_4$: C, 51.01; H, 3.83; N, 9.39%.

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