BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1951—1956 (1971)

Some Oxidation and Reduction Products of 4-Acetyltropolone and Its Methyl Ethers

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(Received February 9, 1971)

The chemical properties of the acetyl side-chain of 4-acetyltropolone and its methyl ethers in relation to some oxidizing and reducing reagents were examined. The selenium-dioxide oxidation of one of the methyl ethers afforded a glyoxyloyl derivative in its hydrate form. The catalytic reduction of 4-acetyltropolone gave a mixture of 4-(1-hydroxyethyl)- and 4-ethyltropolones. The reduction of two isomeric methyl ethers with sodium borohydride gave 4-(1-hydroxyethyl)-2-methoxy- and 6-(1-hydroxyethyl)-2-methoxytropones respectively, from which two isomeric methyl ethers of 4-ethyltropolone were prepared in pure states.

Considering the reactivity of the acetyl group, 4-acetyltropolone (I), which has been obtained by the oxidation of 4-isopropenyltropolone (β-dolabrin),[1] should be expected to be one of the most important materials for the synthesis of troponoid compounds, since no acyltropolone except for formyltropolones[2] has yet been prepared by the direct acylation of tropolones because of the impossibility of the Friedel-Crafts

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[1] T. Nozoe, K. Takase, and M. Ogata, *Chem. & Ind.* (London), **1957**, 1070.

[2] a) E. Sebe and S. Matsumoto, *Sci. Repts. Tohoku Univ., Ser. I.* **38**, 308 (1954); S. Matsumoto, *ibid.*, **42**, 209 (1958). b) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561; W. D. Crow, R. D. Haworth, and P. R. Jefferies, *ibid.*, **1952**, 3705. c) D. S. Tarbell, K. I. H. Williams, and E. J. Sehm, *J. Amer. Chem. Soc.*, **81**, 3443 (1959). d) J. W. Cook, R. A. Raphael, and A. I. Scott, *J. Chem. Soc.*, **1952**, 4416; S. Seto and K. Ogura, This Bulletin, **32**, 493 (1959).

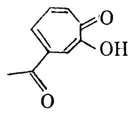
reaction and the related acylation of tropolones.[3] The chemical properties of I, especially those of its acetyl side-chain have been investigated for some reactions — the condensation with arylaldehyde,[1] the Huang-Minlon reduction,[4] the Schmidt reaction,[5] and the ketal formation.[6] The present paper will describe the syntheses of some alkyl ethers of I and the results of the examination of the chemical properties of the acetyl side-chain of I and its methyl ethers in relation to some oxidizing and reducing reagents.

Results and Discussion

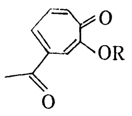
It is known that the tropolone nucleus is broken oxidatively by oxidizing reagents, such as potassium permanganate or chromic acid.[3] On the other hand, although selemium dioxide acts at the tropolone nucleus to give diselenide compounds,[7] this reagent is known to oxidize effectively the methyl side-chain of the methyl ethers of 4-methyltropolone, giving formyl derivatives.[2a] Now, some alkyl ethers of 4-acetyltropolone (I) have been synthesized for the first time and their oxidation with selenium dioxide has been examined.

Because of the highly mobile tautomerism in the tropolone nucleus,[3] tropolones which have substituents at the unsymmetric positions generally should give two kinds of isomeric ethers on *O*-alkylation. The same is true in the case of 4-acetyltropolone (I). Thus, the treatment of silver salt of I with methyl iodide gave a mixture of two isomeric methyl ethers, from which 4-acetyl-2-methoxy- (IIa) and 6-acetyl-2-methoxytropones (IIb) respectively were isolated in crystalline forms. The structures of these ethers were established from the infrared spectral data, showing the characteristic absorptions[8] due to the out-of-plane deformations at 834 and 785 cm^{-1} respectively. The chemical evidence to be presented later also supports these structures. The methylation of I with diazomethane was very complicated; the use of an excess amount of the reagent gave a resinous product, whereas the use of an equimolar amount of the reagent afforded a mixture of IIa and IIb. Two isomeric ethyl ethers, 4-acetyl-2-ethoxy- (IIIa) and 6-acetyl-2-ethoxytropones (IIIb), were also obtained by the treatment of silver salt of I with ethyl iodide. The infrared spectra of these ethers show the characteristic absorptions[8] at 817 and 784 cm^{-1} respectively. Furthermore, isopropyl ethers of I were obtained by the treatment of silver salt of I with isopropyl iodide, but only an isomer, 4-acetyl-2-isopropoxytropone (IVa), was isolated in a crystalline form. Its infrared spectrum shows the characteristic absorption[8] at 825 cm^{-1}. Another isomer, 6-acetyl-2-isopropoxytropone (IVb), was not isolated, but its existence was shown from an absorption at 790 cm^{-1}[8] in the infrared spectrum of the reaction mixture. In the case of the benzylation of I with benzyl chloride, a benzyl ether was isolated in a crystalline form, but its structure could not be determined because of the difficulty in assigning the characteristic absorption due to the out-of-plane deformation in the infrared spectrum.

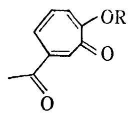
The oxidation of IIa with selenium dioxide in aqueous dioxane gave a compound (V), $C_{10}H_{10}O_5$. The ultraviolet absorption spectrum of V is very similar to that of IIa. The infrared spectrum shows absorptions at 3360, 1096, 1057, and 1037 cm^{-1} associable with the hydroxyl group, in addition to an absorption at 1704 cm^{-1} corresponding to the carbonyl group. From these spectral data, as well as the results of the elementary analysis, V was assigned the structure of 4-(ω,ω-dihydroxyacetyl)-2-methoxytropone, a hydrate form of 4-glyoxyloyl-2-methoxytropone. The further oxidation of V with metaperiodic acid afforded 4-carboxy-2-methoxytropone (VI),[2c] which gave 4-carboxytropolone[2b,9] on hydrolysis with a sodium hydroxide solution. This finding shows that the acetyl side-chain of IIa was oxidized effectively with selenium dioxide. The hydrate, V, was so stable that it did not show any change upon heating at 110°C *in vacuo*. This stability of V is probably due to the inductive effect of the electron-withdrawing tropolone nucleus. In the case of the other isomeric ether, IIb, the treatment with selenium dioxide deposited selenium powder, but no identifiable product could be isolated.



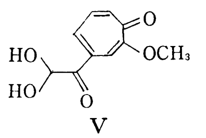
I



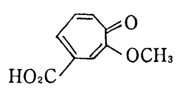
IIa: R=CH_3
IIIa: R=C_2H_5
IVa: R=i-C_3H_7



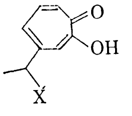
IIb: R=CH_3
IIIb: R=C_2H_5
IVb: R=i-C_3H_7



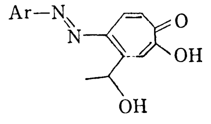
V



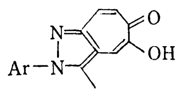
VI



VII: X=OH
VIII: X=H
IX: X=Cl
Xa: X=OCH_3
Xb: X=OC_2H_5



XI: Ar=p-Tolyl



XII: Ar=p-Tolyl

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[3] a) P. L. Pauson, *Chem. Rev.*, **55**, 43 (1955). b) T. Nozoe, *Fortsch. Chem. Org. Naturstoffe*, **13**, 232 (1956).

[4] T. Nozoe, K. Takase, and K. Umino, This Bulletin, **38**, 358 (1965).

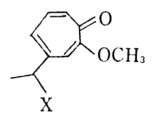
[5] K. Doi, *ibid.*, **34**, 501 (1961).

[6] I. Murata, *ibid.*, **34**, 577 (1961).

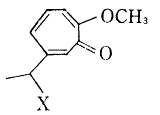
[7] E. Sebe and S. Matsumoto, *Sci. Repts. Tohoku Univ., Ser. I*, **38**, 297 (1954).

[8] 2,4-Disubstituted tropones show the characteristic absorption due to the out-of-plane deformation in the 810—840 cm^{-1} range, and 2,6-disubstituted tropones show it in the 770—800 cm^{-1} range in the infrared spectra; T. Nozoe, K. Takase, and M. Yasunami, to be published.

[9] a) T. Nozoe, Y. Kitahara, and S. Masamune, *Proc. Japan Acad.*, **29**, 17 (1953); T. Nozoe and Y. Kitahara, *ibid.*, **30**, 204 (1954); Y. Kitahara, *Sci. Repts. Tohoku Univ., Ser. I*, **40**, 74 (1956). b) J. R. Bartels-Keith, A. W. Johnson, and W. I. Taylor, *J. Chem. Soc.*, **1951**, 2352.



XIIIa: X=OH
XIVa: X=H
XVa: X=Cl



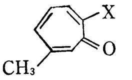
XIIIb: X=OH
XIVb: X=H
XVb: X=Cl

It is known that the tropolone nucleus generally resists catalytic hydrogenation with the palladium-carbon catalyst.[3] The same is true in the case of I. Thus, under similar conditions, the tropolone nucleus of I was not hydrogenated; only the acetyl group was hydrogenated, giving a mixture of 4-(1-hydroxyethyl)-(VII) and 4-ethyltropolone (VIII).[4] The ultraviolet spectrum of VII is similar to that of tropolone, and the infrared spectrum shows an absorption at 3370 cm^{-1} due to the hydroxyl group. The dehydroxylation of VII to VIII was performed effectively by treatment with iodine and red phosphorous in acetic acid. 4-(1-Chloroethyl)tropolone (IX) was derived from VII by treatment with thionyl chloride in the presence of pyridine. The chloro substituent in IX was very sensitive to nucleophilic attack; that is, the treatment of IX with potassium hydroxide in methanol or ethanol afforded 4-(1-methoxyethyl)-(Xa) and 4-(1-ethoxyethyl)-tropolones (Xb) respectively, whose structures were determined from their NMR spectral data. The azocoupling of VII with *p*-toluenediazonium chloride gave an azo compound (XI), which then afforded a 5-hydroxy-6(2*H*)-cyclohepta[*c*]pyrazolone derivative (XII)[10] by cyclization when heated over its melting point or when heated in an alcoholic solution in the presence of hydrochloric acid.

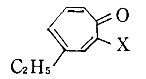
The reaction of I with sodium borohydride gave water-soluble products, but no identifiable compound was isolated from the reaction mixture; this may be a mixture of boron-complexes of the reduction products. On the other hand, the reduction of the methyl ethers, IIa and IIb, with sodium borohydride in aqueous methanol gave the corresponding alcohols, (XIIIa) and (XIIIb) respectively, in good yields. The infrared spectra show absorptions due to the hydroxyl groups at 3360 and 3380 cm^{-1} respectively, and no absorption corresponding to an acetyl carbonyl. On alkaline hydrolysis, both XIIIa and XIIIb gave the same compound, VII, in good yields. Consequently, in oredr to prepare VII conveniently from I, a mixture of the methyl ethers, IIa and IIb, without the separation of each component, could be treated with sodium borohydride and then hydrolyzed with alkali.

The methylation of 4-ethyltropolone (VIII) with diazomethane gave a mixture of two isomeric methyl ethers, 4-ethyl-2-methoxy-(XIVa) and 6-ethyl-2-methoxytropone (XIVb), but the separation of each component from this mixture could not be achieved effectively. However, XIVa and XIVb could be prepared in pure states from XIIIa and XIIIb respectively as follows. The treatment of XIIIa or XIIIb with thionyl chloride in the presence of pyridine gave 4-(1-chloroethyl)-2-methoxy- (XVa) or 6-(1-chloroethyl)-2-methoxytropones (XVb) respectively. Their reductive dechlorinations afforded XIVa and XIVb respectively in good yields.

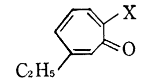
The structures of two series of methyl ethers, IIa, XIIIa, XIVa, and XVa, and IIb, XIIIb, XIVb, and XVb, described above have been presumed only on the basis of a consideration of the infrared spectral data. Now, some chemical evidence for the structural proof of these ethers will be presented. It is known that the reaction of 2-methoxytropones and hydrazine proceeds in the mode of the normal substitution; for example, 2-methoxy-6-methyltropone (XVI) is known to react with hydrazine, giving 2-hydrazino-6-methyltropone (XVII).[11] Moreover, it has now been observed that 6-methyl-2-(*p*-tolylsulfonyloxy)tropone (XVIII)[12] also reacts with hydrazine in a similar manner, giving the same hydrazino compound, XVII.



XVI: X=OCH$_3$
XVII: X=NHNH$_2$
XVIII: X=OTs



XIXa: X=OTs
XXa: X=NHNH$_2$



XIXb: X=OTs
XXb: X=NHNH$_2$

This close relation in the reaction mode between 2-methoxytropone, XVI, and 2-(*p*-tolylsulfonyloxy)-tropone, XVIII, could also be applicable to the structural correlation between the methyl ethers, XIVa and XIVb, and the *p*-tolylsulfonyl derivatives, (XIXa) and (XIXb), of 4-ethyltropolone (VIII) (the structures of the latter have been established).[13] Thus, on treatment with hydrazine, XIVa and XIXa gave the same hydrazino compound (XXa), whereas XIVb and XIXb gave another kind of the same hydrazino compound (XXb). From these facts, the structures of the methyl ethers, XIVa and XIVb, and, consequently, the structures of IIa and IIb were determined by chemical means.

Experimental

All the melting points are uncorrected. The ultraviolet absorption spectra were determined on a Beckman DU spectrophotometer, and the infrared spectra were recorded on a Shimadzu IR-27 infracord apparatus.

Silver Salt of 4-Acetyltropolone (I). Into a solution which had been prepared by the neutralization of I (5.0 g) in water (20 m*l*) with a 0.2 N potassium hydroxide solution (*ca.* 150 m*l*), a solution of silver nitrate (5.1 g) in water (20 m*l*) was stirred. A reddish-orange silver salt immediately precipitated; it was collected by filtration, washed with water, and dried *in vacuo*. Yield, 8.1 g.

Found: C, 38.27; H, 2.44%. Calcd for $C_9H_7O_3Ag$: C, 38.88; H, 2.60%.

4-Acetyl-2-methoxytropone (IIa) and 6-Acetyl-2-methoxytropone (IIb). a) To a suspension of silver salt (8.1 g) of I in dry benzene (150 m*l*), methyl iodide (10 g) was added, and then the mixture was refluxed for 1.5 hr. The silver

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[10] T. Nozoe, K. Takase, and K. Suzuki, This Bulletin, **38**, 362 (1965).

[11] P. Akroyd, R. D. Haworth, and J. D. Hobson, *J. Chem. Soc.*, **1951**, 3427.

[12] T. Sato, *Bull. Chem. Res. Inst. Non-Aqueous Solu., Tohoku Univ.*, **9**, 47 (1959).

[13] T. Nozoe, K. Takase, and T. Sudo, to be published.

iodide thus formed was filtered off, and the benzene filtrate was washed with a 5% sodium hydrogen carbonate solution. After drying over anhydrous sodium sulfate, the evaporation of the solvent left crystals (2.5 g), mp 79—87°C. The sodium hydrogen carbonate solution was extracted with chloroform; the subsequent evaporation of the solvent gave further crops of crystals (2.8 g), mp 76—85°C. The fractional recrystallization of these crystals from ethyl acetate gave IIa as light brown micro-crystals, mp 122.5°C, and IIb as yellow needles, mp 107°C.

Found for IIa: C, 67.64; H, 5.33%. Found for IIb: C, 67.38; H, 5.39%. Calcd for $C_{10}H_{10}O_3$: C, 67.40; 5.66%. UV (MeOH) for IIa: λ_{max} nm (log ε); 250 (4.46), 309 (3.69), 322 (3.68), 369 (3.26). UV (MeOH) for IIb: λ_{max} nm (log ε); 245 (4.44), 310 (3.77), 372 (3.68).

b) To a stirred suspension of I (328 mg) in ether (5 ml), we added a slight excess of an ethereal solution of diazomethane at 0—5°C. The crystals thus formed were collected by filtration, affording a mixture (258 mg) of IIa and IIb.

4-Acetyl-2-ethoxytropone (IIIa) and 6-Acethyl-2-ethoxytropone (IIIb). Silver salt (1.36 g) of I was treated with ethyl iodide (1.56 g) in a manner similar to that described above; the crystals (901 mg), mp 55—62°C, thus obtained were fractionally recrystallized from ether, giving IIIa as yellow needles, mp 88.5—89°C and IIIb as yellow needles, mp 91—92°C.

Found for IIIa: C, 68.52; H, 6.01%. Found for IIIb: C, 68.69; H, 6.05%. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%. UV (MeOH) for IIIa: λ_{max} nm (log ε); 250 (4.52), 310 (3.74), 370 (3.82). UV (MeOH) for IIIb: λ_{max} nm (log ε); 247 (4.49), 315 (3.87), 377 (3.74).

4-Acetyl-2-isopropoxytropone (IVa) and 6-Acetyl-2-isopropoxytropone (IVb). Silver salt (2.71 g) of I was treated with isopropyl iodide (2.2 g) in a manner similar to that described above, and the oily mixture (1.32 g) thus obtained was dissolved in ether, passed through an alumina column, and eluted with ether. The fractions crystallized were collected and recrystallized from petroleum ether, giving IVa as yellow prisms, mp 71—72°C.

Found: C, 69.91; H, 6.80%. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%. UV (MeOH): λ_{max} nm (log ε); 252 (4.52), 310 (3.78), 325 (3.76), 370 (3.84).

The mother liquor of recrystallization did not crystallize, but its infrared spectrum shows an absorption at 790 cm^{-1}, corresponding to the characteristic absorption[8)] for 6-acetyl-2-isopropoxytropone (IVb).

Benzyl Ether of I. Silver salt (820 mg) of I was treated with benzyl chloride (460 mg) in a manner similar to that described above; the crystals (230 mg) thus obtained were recrystallized from ethyl acetate, giving benzyl ether as orangish yellow prisms, mp 177°C.

Found: C, 75.85; H. 5.39%. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%. UV (MeOH): λ_{max} nm (log ε); 237 (4.44), 320 (2.83).

4-(ω,ω-Dihydroxyacetyl)-2-methoxytropone (V). A mixture of IIa (712 mg) and selenium dioxide (490 mg) in dioxane (3 ml) containing a small amount of water (0.1 ml) was refluxed for 5 hr. The selenium thus deposited was filtered off, and the filtrate was allowed to stand at room temperature. The crystals thus formed were collected by filtration and recrystallized from dimethylformamide, giving V as fine, organish-yellow leaflets, mp 144—146°C.

Found: C, 56.93; H, 4.48%. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80%. UV (MeOH): λ_{max} nm (log ε); 248 (4.41), 322 (3.76), 350 (3.77).

4-Carboxy-2-methoxytropone (VI). To a suspension of V (105 mg) in a mixture of ethanol (4 ml) and water (0.5 ml), metaperiodic acid dihydrate (125 mg) was added. After being stirred for 3 hr at room temperature, the mixture was diluted with water and allowed to stand at room temperature. The crystals thereby formed were collected by filtration to give crude VI (19 mg). The extraction of the filtrate with ethyl acetate gave further crops of VI (77 mg). Recrystallization from 25% aqueous methanol afforded light brown micro-crystals, mp 245°C. The melting point reported[2c)] is 254°C.

Found: C, 60.04; H, 4.57%. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48%. UV (MeOH): λ_{max} nm (log ε); 245 (4.45), 323 (3.82), 360 (3.83). The infrared spectrum shows sbsorptions at 2700—2500 and 1721 cm^{-1} (carboxyl).

The hydrolysis of VI by warming it with a dilute sodium hydroxide solution gave 4-carboxytropolone, mp 215°C. The melting point reported [2b)] is 217°C.

Catalytic Reduction of 4-Acetyltropolone (I). A solution of I (3.0 g) in methanol (50 ml) was shaken, in the presence of 5% palladium-carbon, under a hydrogen atmosphere; 850 ml of hydrogen gas were consumed in a period of 15 hr at 18°C. The removal of the palladium catalyst and of the solvent left an oily material, to which a small amount of benzene was added; the mixture was then allowed to stand. The crude crystals (1.07 g), mp 85—89°C, thereby formed were collected by filtration. Recrystallization from ethyl acetate afforded 4-(1-hydroxyethyl)tropolone (VII) as pale yellow prisms, mp 97—98°C.

Found: C, 65.30; H, 6.21%. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07%. UV (MeOH): λ_{max} nm (log ε); 240 (4.45), 322 (3.86), 350 (3.77).

The filtrate was passed through a silica gel column and eluted with benzene. The removal of the solvent from the effluent gave an oily substance (600 mg). Distillation *in vacuo* and then recrystallization from petroleum ether gave 4-ethyltropolone (VIII) as colorless rhombic prisms, mp 42—43°C.

4-Ethyltropolone (VIII) from 4-(1-Hydroxyethyl)tropolone (VII). A mixture of VII (160 mg), iodine (50 mg), and red phosphorous (150 mg) in acetic acid (2 ml) containing a small amount of water (0.5 ml) was refluxed for 4 hr. A precipitate was filtered off, and the filtrate was diluted with water and then extracted with chloroform The removal of the solvent left an oily substance, which was distilled *in vacuo* and crystallized on being allowed to stand, giving VIII (130 mg). Recrystallization from petroleum ether gave colorless rhombic prisms, mp 42—43°C.

4-(1-Chloroethyl)tropolone (IX). To a solution of VII (340 mg) and pyridine (160 mg) in dry dioxane (3 ml), we added a solution of thionyl chloride (400 ml) in dry dioxane (2 ml); the mixture was then stirred for 5 hr at room temperature. After the removal of the solvent, the residue was recrystallized from petroleum ether, giving IX (260 mg) as yellow needles, mp 82—83°C.

Found: C, 58.53; H, 4.65%. Calcd for $C_9H_9O_2Cl$:C, 58.55; H, 4.91%. UV (MeOH): λ_{max} nm (log ε); 341 (4.48), 324 (3.85), 355 (3.75).

4-(1-Methoxyethyl)tropolone (Xa). A solution of IX (185 mg) in methanol (2 ml) containing a 6 N potassium hydroxide solution (1 ml) was refluxed for 2.5 hr. The reaction mixture was then diluted with water (20 ml), acidified with 6 N hydrochloric acid, extracted with benzene, and dried over anhydrous sodium sulfate. The evaporation of the solvent left crystals (185 mg) which were subsequently recrystallized from cyclohexane, giving Xa (150 mg) as colorless prisms, mp 65—66°C.

Found: C, 66.91; H, 6.41%. Calcd for $C_{10}H_{12}O_3$; C, 66.65; H, 6.71%. UV (MeOH): λ_{max} nm (log ε); 238 (4.46), 325 (4.17), 367 (3.98). NMR ($CDCl_3$): δ ppm; 1.42 (3H,d, J=6.5 Hz, $C\underline{H}_3$-CH), 3.27 (3H, s, CH_3O–), 4.20 (1H, q, J=6.5 Hz, CH_3-$\dot{C}\underline{H}$-O), 6.93-7.46 (4H, m, ring protons).

4-(1-Ethoxyethyl)tropolone (Xb). To a solution of IX (550 mg) in ethanol (2 m*l*) we added a potassium hydroxide solution (6 m*l*) which had been prepared by dissolving potassium hydroxide (10 g) in a mixture of water (10 m*l*) and ethanol (40 m*l*), and then the mixture was refluxed for 2 hr. The reaction mixture was diluted with water (10 m*l*), acidified with 6 N hydrochloric acid, extracted with chloroform, and dried over anhydrous sodium sulfate. The evaporation of the solvent left a light brown, oily material (270 mg). This was dissolved in ether and chromatographed on a silica gel column. The first fraction, when eluted with ether, gave Xb (193 mg), mp 58—62°C. The second fraction gave the same compound (50 mg), mp 56—60°C. Recrystallization from cyclohexane afforded colorless prisms, mp 63—64°C.

Found: C, 68.00, H, 7.06%. Calcd for $C_{11}H_{14}O_3$, C, 68.02. H, 7.27%. UV (CH_3OH), λ_{max} nm (log ε); 238 (4.45), 325 (3.97), 365 (3.75). NMR ($CDCl_3$): δ ppm, 1.34 (3H, t, J=7.0 Hz, $C\underline{H}_3$-CH_2), 1.42 (3H, d, J=6.5 Hz, $C\underline{H}_3$-CH), 3.42 (2H, q, J=7.0 Hz, $CH_3C\underline{H}_2$-O–), 4.34 (1H, q, J=6.5 Hz, CH_3-$\dot{C}\underline{H}$-O), 6.93—7.46 (4H, ring protons).

*4-(1-Hydroxyethyl)-5-(*p*-tolylazo)tropolone (XI).* To a solution of VII (160 mg) in pyridine (0.7 m*l*) we added a solution of *p*-toluenediazonium chloride which had been prepared by the diazotization of a solution of *p*-toluidine (120 mg) in water (1 m*l*) containing a 6N hydrochloric acid (0.5 m*l*) with a solution of sodium nitrite (80 mg) in water (0.5 m*l*), with stirring under cooling with ice-water. Water was added to the mixture, and the crystals thereby deposited were collected by filtration and recrystallized from benzene, giving XI (240 mg) as orange needles. These needles evolved gas at 123—126°C and melted at 202—204°C.

Found: C, 67.19; H, 5.34; N, 9.61%. Calcd for $C_{16}H_{16}O_3N_2$: C, 67.59; H, 5.67; N, 9.85%. UV (MeOH): λ_{max} nm (log ε); 232 (4.37), 300 (3.99), 397 (4.41).

*5-Hydroxy-3-methyl-2-(*p*-tolyl)-6(2*H*)-cyclohepta[*c*]pyrazolone (XII).* A mixture of XI (100 mg) in ethanol (10 m*l*) containing 6N hydrochloric acid (0.3 m*l*) was refluxed for 2 hr and then allowed to cool, giving XII (70 mg) as pale yellow needles, mp 203—204°C.[10)]

4-(1-Hydroxyethyl)-2-methoxytropone (XIIIa). To a solution of IIa (160 mg) in 10% aqueous methanol (2 m*l*), sodium borohydride (40 mg) was added; the mixture was stirred for 1 hr at room temperature, and then diluted with water and extracted with ethyl methyl ketone. The extract was dried over anhydrous sodium sulfate; the subsequent evaporation of the solvent left crystals (150 mg), mp 118—120°C. Recrystallization from ethyl acetate gave XIIIa as colorless micro-needles, mp 121—122°C.

Found: C, 66.60; H, 6.42%. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%. UV (MeOH): λ_{max} nm (log ε); 241 (4.46), 320 (3.88), 345 (3.92).

6-(1-Hydroxyethyl)-2-methoxytropone (XIIIb). The treatment of IIb (270 mg) in a manner similar to that described above gave XIIIb (180 mg) as colorless micro-needles, mp 139°C.

Found: C, 66.25; H, 6.43%. Calcd for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71%. UV (MeOH): λ_{max} nm (log ε); 239 (4.43), 319 (3.70).

Hydrolysis of XIIIa and XIIIb. A solution of XIIIa (180 mg) in a 2N potassium hydroxide solution (2 m*l*) was refluxed for 1 hr; then it was diluted with water, acidified with 6N hydrochloric acid, and extracted with ethyl methyl ketone. The evaporation of the solvent gave VII (160 mg), mp 93—96°C. A similar treatment of XIIIb (180 mg) gave VII (160 mg), mp 95—97°C.

4-(1-Chloroethyl)-2-methoxytropone (XVa). To a solution of XIIIa (360 mg) in chloroform (3 m*l*) containing pyridine (180 mg), a solution of thionyl chloride (260 mg) in chloroform (1 m*l*) was added, drop by drop, at room temperature. After being stirred for 3 hr and then allowed to stand overnight, the mixture was washed with water and dried over anhydrous sodium sulfate. The evaporation of the solvent gave an oily XVa (311 mg). A sample for the elementary analysis was prepared by distillation *in vacuo.*

Found: C, 59.98; H, 5.36%. Calcd for $C_{10}H_{11}O_2Cl$: C, 60.46; H, 5.58%. UV (MeOH): λ_{max} nm (log ε); 243 (4.26), 330 (3.72).

6-(1-Chloroethyl)-2-methoxytropone (XVb). The treatment of XIIIb (180 mg) in a manner similar to that described above gave XVb (158 mg). Recrystallization from ethyl acetate gave colorless prisms, mp 85—86°C.

Found: C, 60.90; H, 5.39%. Calcd for $C_{10}H_{11}O_2Cl$: C, 60.46; H, 5.58%. UV (MeOH): λ_{max} nm (log ε); 242 (4.38), 325 (3.76).

4-Ethyl-2-methoxytropone (XIVa). A mixture of XVa (202 mg), 5% palladium-carbon (10 mg), and sodium acetate (90 mg) in methanol (6 m*l*) was subjected to hydrogenolysis at room temperature. The reaction was stopped when an equimolar amount of hydrogen gas had been uptaken. After the removal of the catalyst and of the solvent, the mixture was diluted with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate, and the solvent was evaporated, giving XIVa (168 mg) as a pale yellow oil. A sample for the elementary analysis was prepared by distillation *in vacuo.*

Found: C, 69.67; H, 7.10%. Calcd for $C_{10}H_{12}O_2\cdot\frac{1}{2}H_2O$: C, 69.34; H, 7.57%. UV (MeOH): λ_{max} nm (log ε); 242 (4.38), 325 (3.76).

6-Ethyl-2-methoxytropone (XIVb). A mixture of XVb (90 mg), 5% palladium-carbon (20 mg), and sodium acetate (45 mg) in methanol (5 m*l*) was treated as has been described above, giving XIVb (73 mg). Recrystallization from petroleum ether afforded colorless needles, mp 53—55°C.

Found: C, 73.26; H, 7.10%. Calcd for $C_{10}H_{12}O_2$; C, 73.14; H, 7.37%. UV (MeOH): λ_{max} nm (log ε); 239 (4.44), 325 (3.86).

Picrate: Yellow crystals (from ethanol); mp 140—141°C.

Found: C, 48.70; H, 3.77; N, 10.80%. Calcd for $C_{16}H_{15}O_9N_3$: C, 48.86; H, 3.84; N, 10.68%.

2-Hydrazino-6-methyltropone (XVII). *a) From 2-Methoxy-6-methyltropone (XVI)*: A mixture of XVI (300 mg) and 80% hydrazine hydrate (250 mg) in water (0.5 m*l*) was heated for 5 min at 100°C, and then allowed to cool, giving XVII (250 mg) as yellow needles, mp 123—124°C. The melting point reported[11)] is 134—135°C.

*b) From 6-Methyl-2-(*p*-tolylsulfonyloxy)tropone (XVIII)*: A similar treatment of XVIII (290 mg) with 80% hydrazine hydrate (250 mg) in methanol gave yellow needles, mp 123—124°C, which were identical with XVII.

4-Ethyl-2-hydrazinotropone (XXa). *a) From 4-Ethyl-2-(*p*-tolylsulfonyloxy)tropone (XIXa)*: A mixture of XIXa (218 mg) and 80% hydrazine hydrate (1 m*l*) in methanol (1 m*l*) was heated for 10 min at 100°C. The mixture was diluted with water and extracted with ether, and then the ether solution was passed through an alumina column. The evaporation of the solvent from the effluent gave XXa (100 mg) as a reddish oil.

Found: C, 65.80; H, 7.25; N, 17.42%. Calcd for $C_9H_{12}ON_2$: C, 65.83, H, 7.37; N, 17.06%.

b) From 4-Ethyl-2-methoxytropone (XIVa): A similar treatment of XIVa (40 mg) with 80% hydrazine hydrate (0.5 m*l*) gave a reddish oily material (35 mg) which was identical with XXa.

*6-Ethyl-2-hydrazinotropone (XXb). a) From 6-Ethyl-2-(*p*-tolylsulfonyloxy)tropone (XIXb)*: A mixture of XIXb (218 mg) and 80% hydrazine hydrate (1 m*l*) in methanol (1 m*l*) was treated as has been described above. The crystals (16 mg), mp 64—67°C, thus obtained were recrystallized from ether, giving XXb as orange needles, mp 71—72°C.

Found: C, 65.72; H, 7.18; N, 16.86%. Calcd for $C_9H_{12}ON_2$: C, 65.83; H, 7.37; N, 16.06%.

b) From 6-Ethyl-2-methoxytropone (XIVb): A similar treatment of XIVb (20 mg) with 80% hydrazine hydrate gave yellow crystals (18 mg), mp 69—72°C. Recrystallization from ether gave yellow prisms, mp 71—72°C, which were identical with XXb.

The authors wish to thank the Takasago Perfumery Co., Ltd., for its assistance in the preparation of the β-dolabrin.