In addition, Cosgrove and Waters,[6] Yohe and Hill,[7] and Moore and Waters[8] proposed (A) as the intermediate of (M_4) from BHT in the reaction with various oxidizing agents, while Cook[9] and Fujisaki[10] estimated (B) as this intermediate. With consideration of these data, it is interesting that BHT-alc changed to a dimer *in vivo*.

On the determination of antioxidative effect on concentrated vitamin A oil, BHT-alc and BHT-alc-Me (oxidation products of BHT) showed an excellent effect like BHT. Previously, Cook[9] reported that BHT-diphenylethane also exhibited an excellent effect.

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Summary

3,5-Di-*tert*-butyl-4-hydroxy-benzoic acid, 4,4′-ethylenebis(2,6-di-*tert*-butylphenol), and unchanged α-hydroxy-2,6-di-*tert*-butyl-*p*-cresol were isolated and characterized from the urine of a rabbit dosed with α-hydroxy-2,6-di-*tert*-butyl-*p*-cresol. The isolated 3,5-di-*tert*-butyl-4-hydroxy-benzaldehyde was identified as its 2,4-dinitrophenylhydrazone. A glucuronide was isolated as its triacetyl-methyl ester. Antioxidative effect of 2,6-di-*tert*-butyl-*p*-cresol and its derivatives on vitamin A was examined.

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UDC 547.834.3.07

34. Masao Shimizu, Fumihiko Uchimaru, and Bumpei Kurihara: Studies on N-Substituted Nortropane Derivatives. V.[1] High-pressure Catalytic Hydrogenation of N-Substituted 3-Nortropanones and their Methiodides.

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As described in Part II[2] of this series, one of the authors obtained the epimeric mixture of alcohols, 3α(axial)- and 3β(equatorial)-ols, by sodium borohydride reduction of several kinds of N-substituted 3-nortropanone derivatives. The present paper describes further studies on these 3-ketones and their methiodides.

Keagle and Hartung[3] obtained 3α-tropanol by the reduction of 3-tropanone over platinum oxide, and Stoll, *et al.*[4] reported the formation of corresponding 3α-ols by the reduction of various N-substituted 6-hydroxy(or alkoxy)-3-nortropanone derivatives. In

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1) Part IV: This Bulletin, **9**, 313 (1961).
2) Part II: *Ibid.*, **9**, 304 (1961).
3) L. C. Keagle, W. H. Hartung: J. Am. Chem. Soc., **68**, 1608 (1946).
4) A. Stoll, E. Jucker: Angew. Chem., **66**, 376 (1954).

the present work, reduction was carried out essentially under the same condition as that of Stoll, *et al.*, with initial hydrogen pressure of 60 kg./cm^2, at 40~50° for 5 hours, over freshly prepared Raney nickel W-5. The fractions separated from the reaction mixture by chromatography were checked for the presence of corresponding 3β-ols by infrared absorption spectra, as described in Part III.[5] There was no indication of the presence of 3β-ols in the reduction products and only 3α-ols were detected by infrared spectra. The separated 3α-ols and also their derivatives were identified with authentic specimens by mixed fusion. Table I gives the yield of 3α-ols and also shows that the change of substituted groups (R) at N has no influence on the course of reduction except the compound No. 4 (R=-CH_2COOH).

Table I. High-pressure Catalytic Hydrogenation of N-Substituted 3-Nortropanones

Compd. No.	N-R	Yield (%)		
		Product (3α-ol)	Recovered material	Total
1	N-CH_3	93.7		93.7
2	N-CH_2CH_2OH	88.0	(4.0)	92.0
3	N-$CH_2COOC_2H_5$	77.2		77.2
4	N-CH_2COOH		89.3	89.3

Catalytic reduction of 3-tropanone does not give the corresponding 3β-ol but 3α-ol, which is explained by steric hindrance of ethylene bridge close to C-3 carbonyl group, as discussed earlier by Beckett, *et al.*[6] Present experiment shows exclusive formation of 3α-ols in the reduction of N-substituted 3-nortropanones possessing a more bulky group than methyl, such as 2-hydroxyethyl or ethoxycarbonylmethyl. In general it may be said that N-substituted 3-nortropanone takes four possible conformations in solution as shown in Chart 1. Many discussions[7] have been made in the past concerning the

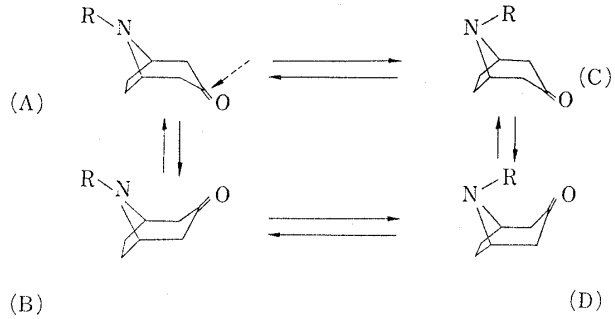

Chart 1.

conformation of N-substituent of tropane, but it may be considered that the interconversion between axial and equatorial orientation occurs readily in solution. According to Closs' discussion[7] or Mckenna's review,[8] it is reasonable to assume that (A) type must be the most stable. The reduction might be considered to proceed from the side of ----→ in (A) form.

Fodor[9] established the conformation of N-substituents in quaternary salt of tropane

5) Part III : This Bulletin, **9**, 308 (1961).
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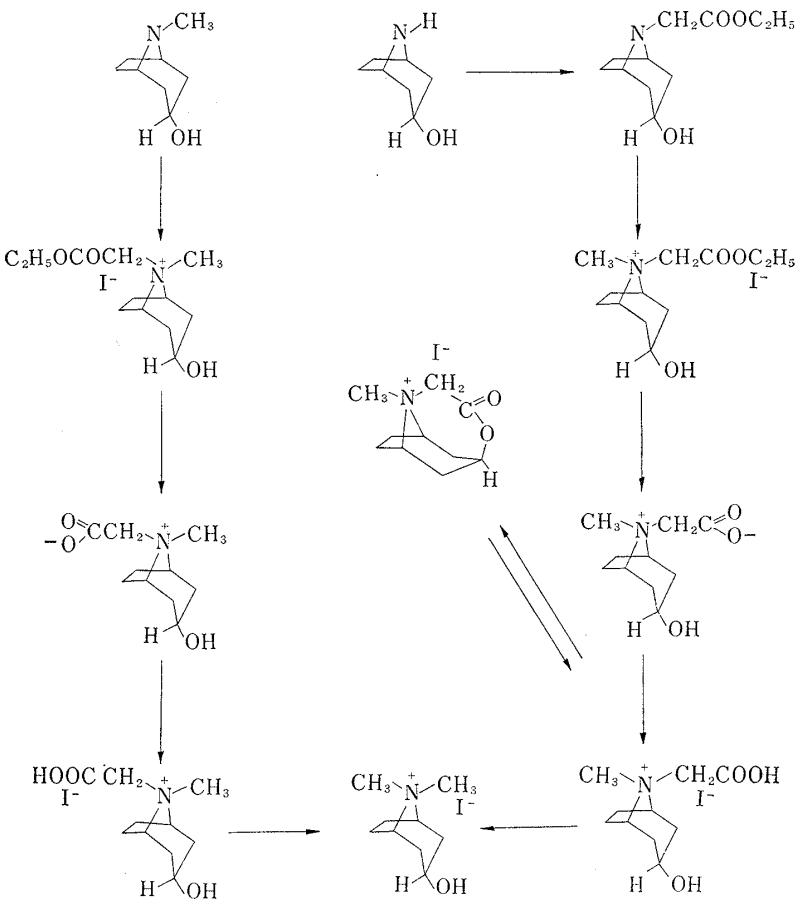

Chart 2.

on the ground of a series of experiments shown in Chart 2. Attempt was then made to reduce, under the same condition as above, N-substituted 3-nortropanone methiodides possessing a bulky group, such as 2-hydroxyethyl or ethoxycarbonylmethyl, on N_a side (piperidine side), stereochemistry of which was discussed by Fodor.

Before the reduction, infrared spectra of above quaternary salts were taken to

Table II. N-Substituted 3-Nortropanone Methiodides

Compd. No.	R_2 (N_b)	R_1 (N_a)	m.p. (°C) (decomp.)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1	CH_3	CH_3	273~274	$C_9H_{16}ONI$	38.45	5.74	4.98	38.53	5.61	4.48
2	CH_3	CH_2CH_2OH	222~223	$C_{10}H_{18}O_2NI$	38.60	5.84	4.50	38.48	5.70	4.66
3	CH_3	$CH_2COOC_2H_5$	189~190	$C_{12}H_{20}O_3NI$	40.81	5.71	3.96	40.63	5.59	4.31
4	$CH_2COOC_2H_5$	CH_3	200~201	$C_{12}H_{20}O_3NI$	40.81	5.71	3.96	41.02	5.90	3.54

Table III. Infrared Spectra of N-Substituted 3-Nortropanone Methiodides

Compd. No.	R_2 (N_b)	R_1 (N_a)	Absorption (cm^{-1}) $\nu_{C=O}$	$CO-CH_2-$	δ_{CH}	ν_{C-N}	[a]
1	CH_3	CH_3	1728	1417	1355	1024	1497
2	CH_3	CH_2CH_2OH	1716	1417	1355	1024	1500
3	CH_3	$CH_2COOC_2H_5$	(1737)[b]	1427	1354	1028	1494
4	$CH_2COOC_2H_5$	CH_3	1731	1423	1353	1023	(1496)

a) For this absorption see K. Zeile, W. Schulz: Ber., 88, 1078 (1955).
b) This absorption overlaps that of ester carbonyl.

compare with those of their reduction products which were presumably very difficult to purify. Tables II and III show melting points and infrared absorption bands of N-substituted 3-nortropanone methiodides. In the case of tertiary amines, the $\nu_{C=O}$ appeared in the range of 1708~1715 cm^{-1} as a six-membered ring ketone. In the spectra of the methiodides, frequency of the ketone shifted somewhat to a higher wave-number region and the shift was presumed to be the result of a greater strain of piperidine ring by quaternization. Tables IV and V show melting points and various absorption bands of

Table IV. Quaternary Salts of N-Substituted 3α- and 3β-Nortropanols

Compd. No.	R_2 (N_b)	R_1 (N_a)	C-3 O-H	X	m.p. (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1	CH_3	CH_3	a	I	344~345 (decomp.)	$C_9H_{18}ONI$	38.17	6.41	4.95	38.14	6.19	4.93
2	CH_3	CH_3	e	I	337~338 (decomp.)	$C_9H_{18}ONI$	38.17	6.41	4.95	38.14	6.19	5.54
3	CH_3	CH_2CH_2OH	a	I	290<	$C_{10}H_{20}O_2NI$	38.35	6.44	4.47	38.74	6.46	4.92
4	CH_3	CH_2CH_2OH	e	I	288~289 (decomp.)	$C_{10}H_{20}O_2NI$	38.35	6.44	4.47	38.96	6.43	4.38
5	CH_3	$CH_2COOC_2H_5$	a	I	214~215 (decomp.)	$C_{12}H_{22}O_3NI$	40.54	6.24	3.94	40.81	6.16	3.70
6	$CH_2COOC_2H_5$	CH_3	a	I	214~215 (decomp.)	$C_{12}H_{22}O_3NI$	40.54	6.24	3.94	41.03	6.08	3.68
7	CH_3	$CH_2COOC_2H_5$	e	I	204~206 (decomp.)	$C_{12}H_{22}O_3NI$	40.54	6.24	3.94	40.66	6.44	4.08
8	CH_3	$CH<^{CH_3}_{COOC_2H_5}$	a	I	158~160	$C_{13}H_{24}O_3NI$	42.28	6.55	3.79	42.29	6.59	3.39
9	CH_3	$CH<^{CH_3}_{COOC_2H_5}$	e	I	184~185	$C_{13}H_{24}O_3NI$	42.28	6.55	3.79	42.78	6.11	3.84
10	CH_2COOCH_3	CH_3	a	Br	179~181	$C_{11}H_{20}O_3NBr$	44.91	6.85	4.76	45.30	6.93	4.87
11	CH_3	CH_2COOCH_3	a	Br	190~193 (decomp.)	$C_{11}H_{20}O_3NBr$	44.91	6.85	4.76	44.72	6.82	4.51
12	CH_2COOCH_3	CH_3	e	Br	212~213 (decomp.)	$C_{11}H_{20}O_3NBr$	44.91	6.85	4.76	44.81	7.27	4.64

Table V. Infrared Spectra of Quaternary Salts of N-Substituted 3α- and 3β-Nortropanols

Compd. No.	R_2 (N_b)	R_1 (N_a)	C-3 O-H	X	Absorptions (cm^{-1}) Hydroxyl ν_{O-H}	Hydroxyl ν_{C-O}	Ester $\nu_{C=O}$	Ester ν_{C-N}	a)
1	CH_3	CH_3	a	I	3370	1052		1009	1488
2	CH_3	CH_3	e	I	3335	1085		1025	1501
3	CH_3	CH_2CH_2OH	a	I	3350	1047			1485
4	CH_3	CH_2CH_2OH	e	I	3330	1070		1027	1495
5	CH_3	$CH_2COOC_2H_5$	a	I	3360	1050	1737	1026	1487
6	$CH_2COOC_2H_5$	CH_3	a	I	3390	1050	1740	1025	
7	CH_3	$CH_2COOC_2H_5$	e	I	3345	1077	1742	1018	1500
8	CH_3	$CH<^{CH_3}_{COOC_2H_5}$	a	I	3350	1047	1738	1005	1487
9	CH_3	$CH<^{CH_3}_{COOC_2H_5}$	e	I	3325	1075	1736	1009	1497
10	CH_2COOCH_3	CH_3	a	Br	3370	1050	1756	1016	1490
11	CH_3	CH_2COOCH_3	a	Br	3340	1050	1743		(1488)
12	CH_2COOCH_3	CH_3	e	Br	3280	1080	1746	1010	1502

a) For this absorption see K. Zeile, W. Schulz: Ber., 88, 1078 (1955).

corresponding 3-ols. The regularity of C-O stretching frequencies between two epimers was also observed in this case, as in tertiary amines. Zeile and Schulz[7] reported the infrared spectra of quaternary salts of N-substituted nortropane derivatives but did not referred to the assignment of their absorptions. According to the present measurements,

those possessing an axial hydroxyl group exhibited bands in the range of 1047～1052 cm^{-1}, and those with an equatorial hydroxyl, in the range of 1070～1085 cm^{-1}. Although these absorption have somewhat shifted to the higher frequencies compared with the corresponding tertiary amines, the difference of wave numbers between these two epimers is almost the same 25 cm^{-1} as between epimers of tertiary amines. On the other hand, the stretching vibration of hydroxyl groups appeared in the range of 3280～3370 cm^{-1} (tertiary amines, 3230～3420 cm^{-1}) and the stretching vibration of ester carbonyl at 1736～1756 cm^{-1} (tertiary amines, 1731～1751 cm^{-1}) showed no significant difference of these values between quaternary salts and tertiary amines. In addition to these absorption bands, almost all the quaternary salts show bands at about 1480 cm^{-1} in their spectra. Experimental evidence based on the analysis of the effect of substituents on this band (1480 cm^{-1}) supported the view, which was pointed out by Zeile and Schulz, that the compounds possessing larger substituents at N_a side (piperidine) have higher intensity than those at N_b side (pyrrolidine). The same tendency was observed in the spectra of the three N-isomers. This absorption band is not so intensive as to characterize quaternary salts, but it seems to be available for discussion about them, because these compounds have no other characteristic band in their spectra.

Methiodides were catalytically reduced in a solution of 80% ethanol by the same method as described for the reduction of tertiary amines. Reduction products were purified by fractional recrystallization, examined by infrared spectra, and finally confirmed by the comparison of melting point with authentic samples and elemental analyses, as shown in Table VI. In the case of 3-tropanone methiodide, 84% of crude

Table VI. High-pressure Catalytic Hydrogenation of N-Substituted 3-Nortropanone Methiodides

Compd. No.	$CH_3-\overset{+}{N}(\wedge)-R\ I^-$	Yield (%)		
		Crude methiodide[a]	Product 3α-ol methiodide[b]	Recovered material etc.
1	N-CH_3	84.0	65.4	
2	N-CH_2CH_2OH	59.0	41.4	(33.0)*
3	N-$CH_2COOC_2H_5$	86.6	17.8	24.9

a) Weight % to the starting material (in No. 2, oily substance* was excluded).
b) Theoretical yield to the starting material.

methiodide showing no $\nu_{C=O}$ vibration in its infrared spectrum was obtained and, after recrystallization 65.4% of pure 3α-tropanol methiodide was separated. 8-(2-Hydroxyethyl)-3-nortropanone methiodide yields 59.0% of crude methiodide, besides 33% of oily material. The crude methiodide lacking carbonyl absorption in its infrared spectrum gave 41.4% of pure 3α-hydroxy-8-nortropaneëthanol methiodide. As for the oily substance, it is reasonable to assume that this substance is a mixture of tertiary amines as described in the experimental part. Ethyl 3-oxo-8-nortropaneacetate methiodide yielded 86.6% of crude methiodide which, after fractional recrystallization, gave 17.8% of 3α-ol methiodide and 24.9% of recovered material.

It is very difficult to separate all reduction products quantitatively from the reaction mixture owing to solubility of quaternary salts and the formation of 3β-ol methiodide cannot be denied completely. The yield of 3α-ol methiodides decreased from 65.4% to 17.8% in the reverse order of the size of substituent groups. Therefore, it is possible to assume that the N_a-substituents hinder to some extent the catalytic hydrogenation of C-3 carbonyl group. In view of Fodor's experiment that the N_a-carboxymethyl group can lactonize with 3β-hydroxy group, it is probable that the above-mentioned N_a-substituents are present in a suitable proximity of C-3 carbonyl groups.

Experimental*2

Catalytic Hydrogenation of 3-Tropanone (Tropinone)——Purified 3-tropanone (m.p. 39～43°) (1.00 g.) in dehyd. EtOH (30 cc.) was catalytically hydrogenated over freshly prepared Raney Ni W-5 (0.2 g.) catalyst at 40～50° under a pressure of 60 kg./cm² for 5 hr. The reaction mixture was filtered, the bright yellow oil (1.0 g.), obtained on evaporation of the solvent *in vacuo*, was dissolved in a mixture of Et_2O-benzene (1:1), and chromatographed over Al_2O_3 (20 g.) column. Elution with solvents ranging from Et_2O-benzene (1:1) to $CHCl_3$-MeOH (19:1) gave 950 mg. (93.7%) of a crystalline substance (m.p. 45～50°). The infrared spectra of the first and the last fractions showed the same absorption as that of pure 3α-tropanol (IR $\nu_{max}^{liq.}$ cm^{-1} : ν_{OH} 3340, ν_{C-O} 1046).

In another experiment, the last fraction of Al_2O_3 chromatography was examined by paper partition chromatography (BuOH-HCl-H_2O=9:1:3) and showed only a single spot at Rf 0.33 (control 3α-tropanol, 0.32; 3β-tropanol, Rf 0.22).

Picrate : Yellow prisms, m.p. 268～272°, undepressed with 3α-tropanol picrate, m.p. 272～275°.

8-(2-Hydroxyethyl)-3-nortropanone——8-(2-Hydroxyethyl)-3-nortropanone (1.00 g.) in dehyd. EtOH (30 cc.) was reduced under the same conditions as above. Evaporation of the solvent *in vacuo* gave 1.0 g. of bright yellow oil which was chromatographed on alumina (20 g.) column. Elution with Et_2O-$CHCl_3$ (1:1) gave 40 mg. of oil (recovered crude material from its infrared spectrum) and that with $CHCl_3$-MeOH (9:1) gave 890 mg. (88.0%) of a crystalline substance (m.p. 90～94°). The latter on further purification by alumina chromatography gave colorless needles of m.p. 103～105°, undepressed with pure 3α-hydroxy-8-nortropaneëthanol, m.p. 104～106°.

Methiodide : m.p. above 290°. *Anal.* Calcd. for $C_{10}H_{20}O_2NI$: C, 38.35; H, 6.44; N, 4.47. Found : C, 38.74; H, 6.46; N, 4.92.

Ethyl 3-Oxo-8-nortropaneacetate——Ethyl 3-oxo-8-nortropaneacetate (1.00 g.) in dehyd. EtOH (30 cc.) was treated as above and yielded a bright yellow oil (1.0 g.). Elution with Et_2O on alumina chromatography gave 780 mg. (77.2%) of colorless oil. Its infrared spectrum ($\nu_{max}^{liq.}$ cm^{-1} : 3380 (OH), 1745 (C=O), 1046 (C-O)) was identical with that of ethyl 3α-hydroxy-8-nortropaneacetate.

Methiodide : Colorless feathers, m.p. 213～214° (decomp.), undepressed with ethyl 3α-hydroxy-8-nortropaneacetate methiodide, m.p. 214～215° (decomp.). Mixed melting point with corresponding 3β-ol methiodide of m.p. 204～206° (decomp.) was 194～197° (decomp.).

Further elution with $CHCl_3$-MeOH (1:1) gave 150 mg. of a crystalline mass which, on recrystallization from MeOH, yielded colorless prisms, m.p. 267～269° (decomp.), undepressed with 3α-hydroxy-8-nortropaneacetic acid, m.p. 274～276° (decomp.). IR ν_{max}^{KBr} cm^{-1} : 3370 (OH), 1608, 1398 (COO^-), 1037 (C-O).

3-Oxo-8-nortropaneacetic Acid——3-Oxo-8-nortropaneacetic acid (280 mg.) in EtOH (30 cc.) was reduced over Raney Ni W-5 (0.4 g.) at 35～45° under a pressure of 60 kg./cm² for 3 hr. After filtration and evaporation of the solvent, the residue (250 mg., m.p. ca. 160～162° (decomp.), 89.3%) was recrystallized from MeOH-iso-PrOH to colorless needles, m.p. 162～163° (decomp.), undepressed and showing the same infrared spectrum with starting material. *Anal.* Calcd. for $C_9H_{13}O_3N$: C, 59.00; H, 7.15; N, 7.65. Found : C, 58.48; H, 6.62; N, 7.63.

3-Tropanone Methiodide——3-Tropanone methiodide (1.00 g.) in 80% EtOH (30 cc.) was reduced as above and yielded 840 mg. (m.p. 335～338°) of crude methiodide showing no C=O absorption in its infrared spectrum. Recrystallization from EtOH gave colorless prisms of m.p. ca. 340° (decomp.) (660 mg., 65.4%). On further purification it showed m.p. 340～341° (decomp.), undepressed with 3α-tropanol methiodide, m.p. 344～345° (decomp.). IR ν_{max}^{KBr} cm^{-1} : 3370 (OH), 1052 (C-O). *Anal.* Calcd. for $C_9H_{18}ONI$: C, 38.17; H, 6.41; N, 4.95. Found : C, 38.35; H, 6.43; N, 4.40.

8-(2-Hydroxyethyl)-3-nortropanone Methiodide——8-(2-Hydroxyethyl)-3-nortropanone methiodide (1.00 g.) in 80% EtOH (30 cc.) was reduced under the same conditions and furnished 1.0 g. of semicrystalline mass. After washing with Et_2O-Me_2CO, 590 mg. of white crystals, m.p. ca. 270°, was obtained which did not show infrared absorptions of the starting material. Further recrystallization from MeOH-Me_2CO gave 420 mg. (41.4%) of slightly yellow crystals of m.p. above 290°. Mixed fusion with 3α-hydroxy-8-nortropaneëthanol methiodide also showed m.p. above 290°. *Anal.* Calcd. for $C_{10}H_{20}O_2NI$: C, 38.35; H, 6.44; N, 4.47. Found : C, 38.78; H, 6.05; N, 4.91. IR ν_{max}^{KBr} cm^{-1} : 3330 (OH), 1047 (C-O).

Evaporation of the above Et_2O-Me_2CO washing furnished a bright yellow oil (330 mg.). Beilstein test, (±). IR $\nu_{max}^{liq.}$ cm^{-1} : 3350 (OH), 1705 (C=O), 1045 (C-O).

Picrate : Yellow needles, m.p. 215～217° (mixed melting point with 3-tropanone picrate (m.p. 217～219°), 213～215°).

Ethyl 3-Oxo-8-nortropaneacetate Methiodide——Ethyl 3-oxo-8-nortropaneacetate methiodide (1.05 g.) in 80% EtOH (30 cc.) was hydrogenated in the same way and yielded 910 mg. of crude methio-

*2 All melting points are uncorrected.

dide. By fractional recrystallization from Me_2CO-MeOH, 180 mg.(17.8%) (m.p. 208~210°(decomp.)) and 250 mg. (24.9%) (m.p. 174~176°(decomp.)) of crystals were obtained. The former (IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 1737 (C=O), 1049 (C-O)) on further recrystallization gave colorless prisms, m.p. 214~215° (decomp.), undepressed with ethyl 3α-hydroxy-8-nortropaneacetate methiodide (m.p. 214~215°(decomp.)). *Anal.* Calcd. for $C_{12}H_{22}O_3NI$: C, 40.54; H, 6.24; N, 3.94. Found: C, 41.07; H, 5.87; N, 4.16.

The latter (IR ν_{max}^{KBr}: 1737 cm^{-1}(C=O in ester and ketone)) on further purification furnished colorless feathers, m.p. 189~190°(decomp.), identical with the starting material on mixed fusion. *Anal.* Calcd. for $C_{12}H_{20}O_3NI$: N, 3.96. Found: N, 4.09.

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Summary

High-pressure catalytic hydrogenation of N-substituted 3-nortropanones reported in Part I of this series and also of their methiodides was examined. In the case of tertiary amines, only the corresponding 3α-ols were obtained as the main product and the influence of N-substituents was not observed. Before the reduction of methiodides, the necessary infrared spectra were measured in order to establish the purity of the products and recovered materials. In reduction of methiodides, the more bulky the N-substituent became, the smaller did the amounts of 3α-ol methiodides. The possibility of a steric hindrance by fixed N_a (piperidine side) substituents in the reduction was discussed.

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35. Tadakazu Tsuji, Taka Nakata, and Takeo Ueda: Synthesis and Antimicrobial Activity of 1-Acyl-2-sulfanilylhydrazine and 1-Acyl-2-(4-amino-1-naphthylsulfonyl)hydrazine.

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In a previous report,[1] it was shown that N-(4-acetamido-1-naphthylsulfonyl)dodecanamide was potentiated as to its effect on the Nakayama strain of Japanese B encephalitis virus by the addition of an acid hydrazide such as anthranilic acid hydrazide or aspartic acid hydrazide. This finding suggested the introduction of a hydrazino group into the basic structure of N-acyl-4-acylamino-1-naphthalenesulfonamide.

Thus, 1-acyl-2-sulfanilylhydrazine, 1-acyl-2-(4-amino-1-naphthylsulfonyl)hydrazine and their acyl derivatives were synthesized and their effect on several pathogenic microbes was examined. This paper describes the synthesis and antimicrobial activity of 1-acyl-2-sulfanilylhydrazine and 1-acyl-2-(4-amino-1-naphthylsulfonyl)hydrazine.

Synthesis of 1-(N-Acetylsulfanilyl)-2-acylhydrazine

Among the compounds of 1-(N-acetylsulfanilyl)-2-acylhydrazine series, Curtius, *et al.*[2] synthesized N^1-amino-N^4-acetylsulfanilamide by reacting N-acetylsulfanilyl chloride with

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2) Th. Curtius, W. Stoll: J. prakt. Chem., 2, **112**, 217 (1925).