C-Nor-D-homo-5α-pregnane-3β,16β,20α-triol 3,16,20-Triacetate (XIb)——A solution of 50 mg. of XIa in 4 ml. of pyridine and 2 ml. of Ac_2O was heated on a water bath. After 1 hr., the reaction mixture was treated in the usual manner and the product was crystallized from MeOH to C-nor-D-homo-pregnane-3β,16β,20α-triol 3,16,20-triacetate (XIb), m.p. 207~207.5°. *Anal.* Calcd. for $C_{27}H_{42}O_6$: C, 70.10; H, 9.15. Found: C, 70.19; H, 9.15.

The authors are grateful to Dr. K. Takeda, Director of the Shionogi Research Laboratories, for the supply of the starting material. They are also indebted to Dr. K. Morita for kind suggestion regarding the Baeyer-Villiger reaction. Thanks are also due to Mrs. T. Toma and Miss A. Maeda for the elemental analysis.

Summary

Conversion of hecogenin acetate to C-nor-D-homosapogenin and degradation of its spiroketal ring were achieved according to the scheme shown in Chart 1.

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2. Yo Ueda, Hiroshige Yano, and Tsutomu Momose: Infrared Spectra of Phenylsulfonyl Derivatives. (4). The Infrared Spectra of N-Acylsulfonamide Derivatives. (Organic Analysis. XLVIII*1).

(*Institute of Pharmaceutical Sciences, Faculty of Medicine, Kyushu University**2)

In a previous paper[1] of this series, the infrared spectral effect of SO_2 group on the carbonyl absorption was briefly described in several N-acetylsulfonamide derivatives. In this work, the infrared spectra of 44 kinds of N-acylsulfonamide derivatives, in which 31 kinds were newly synthesized, have been measured and their carbonyl absorptions, SO_2 stretching frequencies, S-N stretching frequencies, C-N stretching frequencies and C-CO-N stretching frequencies are discussed.

Results and Discussion

Carbonyl Absorption

N-Acyl-N-substituted-sulfonamide derivatives had their carbonyl absorptions at longer wave length region than N-acylsulfonamide derivatives either in solution or in solid state as shown in Table I.

The significant fact to be pointed here is that some of the crystalline N-acyl-N-substituted-sulfonamide derivatives had splitted carbonyl absorptions when they were measured in solid state as seen in the table, and lost the phenomenon entirely in solution and liquid states.

The typical diagram is shown in Fig. 1.

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*1 Part XLVII: This Bulletin, **11**, 1364 (1963).

*2 Katakasu, Fukuoka (上田 陽, 矢野弘重, 百瀬 勉).

1) T. Momose, Y. Ueda, T. Shoji, H. Yano: This Bulletin, **6**, 669 (1958).

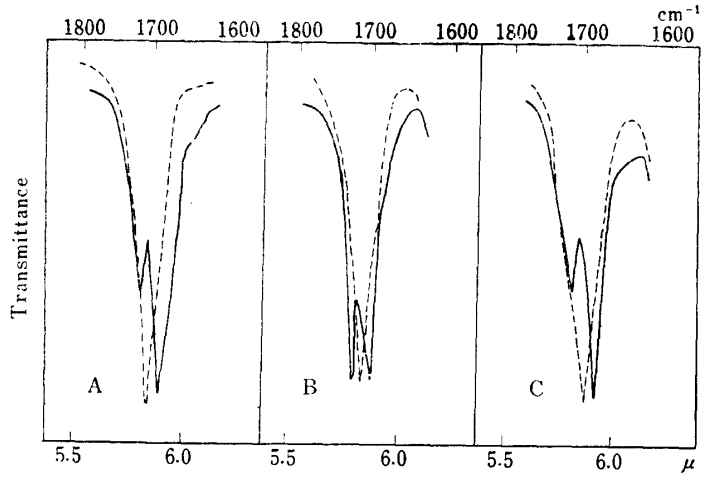


Fig. 1.

—— Nujol mull; ------ in $CHCl_3$
A : $CH_3SO_2N(CH_3)COCH_3$
B : m-$NO_2C_6H_4SO_2N(CH_3)COCH_3$
C : p-$CH_3C_6H_4SO_2N(CH_3)COCH_3$

The remarkable derivatives which had these splitting phenomena were N-acetyl-N-methylsulfonamide derivatives, showing splitted carbonyl absorptions in 7 compounds among 8 crystalline derivatives measured.

Recrystallization of N-acetyl-N-methylethanesulfonamide and N-acetyl-N-methyl-*m*-nitrobenzenesulfonamide from different solvent, resolidification of N-acetyl-N-methyl-*m*-nitrobenzenesulfonamide from fused state, or grinding of N-benzoyl-N-*p*-tolylmethanesulfonamide in a mortar for 2 hr. did not influence upon their carbonyl absorptions.

The splitting phenomena of CO stretching frequency have hitherto been observed in the literature when hydrogen bonding,[2] rotational[3] and conformational[4] isomerism, vibrational coupling,[5] Fermi resonance,[6] intermolecular effects[7] or other effects exert some influence on the spectrum.

Fermi resonance seems to be a reasonable explanation, and actually all N-acetyl-N-methylsulfonamide derivatives which showed splitted carbonyl absorptions had strong absorption bands at about 850 cm^{-1} in solid state. However, N-acetylsulfonamide derivatives generally had strong absorption bands at about 850 cm^{-1}, whereas those compounds showed no splitted carbonyl absorption.*3 This fact makes us hesitate to adopt Fermi resonance to explain the splitting phenomena.

The fact that the splitting phenomenon was not observed in the solution denies the concept of rotational or conformational isomerism, and suggests the possibility of intermolecular effect, however, from our experimental data it was not possible to discuss the nature of intermolecular effect.

It might be difficult to attribute the splitting phenomenon to hydrogen bonding, because N-acyl-N-substituted-sulfonamide derivatives have no hydrogen atom except that of C-H group.

The evidence on hand does not permit to explain the splitting phenomenon unequivocally, but it should be noted that almost all compounds, which showed the splitting

*3 Symmetry elements of those frequencies at about 850 cm^{-1} were not known.

2) *e.g.* : 5β-Pregnane-3β,17α-diol-20-one acetate; R.N. Jones, C. Sandorfy : "Technique of Organic Chemistry," Vol. IX, 488 (1956), Interscience Publ. Inc., New York.

3) *e.g.* : Dihalogen-substituted tertiary amides; L.J. Bellamy : "The Infrared Spectra of Complex Molecules," 213 (1958), Methuen & Co., Ltd., London.

4) *e.g.* : α-Halogenocyclohexanone; E.J. Corey : J. Am. Chem. Soc., **75**, 3297 (1953).

5) *e.g.* : Dicarbonyl compounds.

6) P. Yates, L.L. Williams : J. Am. Chem. Soc., **80**, 5896 (1958).

7) *e.g.* : Long chain hydrocarbons; D. Chapman : J. Chem. Soc,. **1957**, 4489; R.S. Stein : J. Chem. Phys., **23**, 734 (1955).

TABLE I. Wave Numbers of Carbonyl Absorptions and SO_2 Stretching Vibrations

$R^1SO_2N(R^2)COCH_3$					
R^1	R^2		Carbonyl absorption	ν_{SO_2} Asym.	Sym.
CH_3	H	$CHCl_3$	1731	1350	1152
〃	〃	Nujol	1694	1347	1157
〃	CH_3	$CHCl_3$	1714	1366	1160
〃	〃	CS_2	1714	1374	1160
〃	〃	CCl_4	1712	1377	1164
〃	〃	Nujol	1715 1692	1348	1161
〃	C_2H_5	$CHCl_3$	1691	1359	1166
〃	〃	CS_2	1706	1374	1171
〃	〃	liquid	1698	1355	1170
〃	C_3H_7	$CHCl_3$	1695	1359	1164
〃	〃	liquid	1694	1356	1168
〃	C_4H_9	$CHCl_3$	1691	1360	1163
〃	〃	liquid	1694	1355	1167
〃	C_6H_{11}	$CHCl_3$	1700	1369	1166
〃	〃	Nujol	1701	1368	1164
〃	C_6H_5	$CHCl_3$	1705	1369	1164
〃	〃	CS_2	1720	1372	1168
〃	〃	Nujol	1724	1368	1157
〃	p-$C_6H_4CH_3$	$CHCl_3$	1718	1370	1160
〃	〃	Nujol	1700	1350	1161
C_2H_5	H	$CHCl_3$	1730	1348	1148
〃	〃	Nujol	1701	1351	1155
〃	CH_3	$CHCl_3$	1695	1362	1156
〃	〃	CS_2	1709	1370	1153
〃	〃	CCl_4	1706	1370	1157
〃	〃	Nujol	1712 1678	1348	1153
〃	C_2H_5	$CHCl_3$	1691	1360	1150
〃	〃	CS_2	1701	1366	1149
〃	〃	liquid	1695	1352	1149
C_6H_5	H	$CHCl_3$	1733	1355	1161
〃	〃	Nujol	1690	1359	1170
〃	CH_3	$CHCl_3$	1701	1374	1166
〃	〃	CS_2	1712	1376	1167
〃	〃	liquid	1700	1362	1166
p-ClC_6H_4	H	$CHCl_3$	1727	1358	1159
〃	〃	Nujol	1692	1358	1163
〃	CH_3	$CHCl_3$	1703	1373	1165
〃	〃	CS_2	1709	1374	1170
〃	〃	liquid	1700	1370	1170
p-$CH_3C_6H_4$	H	$CHCl_3$	1733	1352	1159
〃	〃	Nujol	1729	1341	1168
〃	CH_3	$CHCl_3$	1695	1373	1166
〃	〃	CS_2	1709	1373	1168
〃	〃	Nujol	1715 1689	1351	1160
〃	C_2H_5	$CHCl_3$	1706	1370	1163
〃	〃	CS_2	1706	1372	1166
〃	〃	Nujol	1748 1706	1350	1166
〃	C_3H_7	$CHCl_3$	1698	1362	1157
〃	〃	Nujol	1695	1351	1159
〃	C_4H_9	$CHCl_3$	1695	1361	1166
〃	〃	Nujol	1698	1359	1160
〃	C_6H_{11}	$CHCl_3$	1689	1363	1166
〃	〃	Nujol	1692	1359	1164
〃	C_6H_5	$CHCl_3$	1712	1374	1168
〃	〃	CS_2	1720	1379	1175

TABLE I. (continued)

$R^1SO_2N(R^2)COCH_3$				ν_{SO_2}	
R^1	R^2		Carbonyl absorption	Asym.	Sym.
p-$CH_3C_6H_4$	C_6H_5	Nujol	1720	1367	1176
〃	*p*-$C_6H_4CH_3$	$CHCl_3$	1711	1374	1167
〃	〃	Nujol	1717	1360	1175
o-$CH_3C_6H_4$	H	$CHCl_3$	1730	1347	1160
〃	〃	Nujol	1688	1355	1174
〃	CH_3	$CHCl_3$	1701	1357	1163
〃	〃	CS_2	1706	1361	1167
〃	〃	liquid	1706	1350	1161
〃	C_2H_5	$CHCl_3$	1692	1358	1160
〃	〃	CS_2	1704	1357	1160
〃	〃	liquid	1698	1348	1157
〃	C_3H_7	$CHCl_3$	1692	1354	1156
〃	〃	liquid	1701	1351	1170
〃	C_4H_9	$CHCl_3$	1697	1357	1164
〃	〃	liquid	1700	1353	1167
〃	C_6H_5	$CHCl_3$	1712	1355	1168
〃	〃	CS_2	1718	1370	1172
〃	〃	Nujol	1709	1346	1233
〃	*p*-$C_6H_4CH_3$	$CHCl_3$	1714	1359	1167
〃	〃	Nujol	1698	1351	1164
p-$CH_3OC_6H_4$	H	〃	1727	1338	1151
〃	CH_3	$CHCl_3$	1692	1368	1159
〃	〃	CS_2	1706	1370	1163
〃	〃	liquid	1698	1361	1153
p-CNC_6H_4	H	Nujol	1715	1348	1153
〃	CH_3	〃	1724 1709	1366	1181
α-$C_{10}H_7$	〃	$CHCl_3$	1701	1362	1160
〃	〃	CS_2	1711	1364	1163
〃	〃	Nujol	1718 1704	1335	1160
β-$C_{10}H_7$	〃	$CHCl_3$	1695	1376	1163
〃	〃	CS_2	1709	1376	1167
〃	〃	Nujol	1708	1373	1170
m-$NO_2C_6H_4$	H	$CHCl_3$	1730	1359	1167
〃	〃	Nujol	1701	1362	1175
〃	CH_3	$CHCl_3$	1714	1359	1170
〃	〃	CS_2	1715	1353	1174
〃	〃	Nujol	1718 1695	1357	1183
〃	C_2H_5	$CHCl_3$	1703	1357	1173
〃	〃	CS_2	1712	1353	1183
〃	〃	Nujol	1695	1364	1176
〃	C_3H_7	$CHCl_3$	1701	1361	1175
〃	〃	Nujol	1697	1362	1176
〃	C_6H_5	$CHCl_3$	1709	1360	1173
〃	〃	CS_2	1721	1353	1182
〃	〃	Nujol	1709	1359	1186
〃	C_4H_9	$CHCl_3$	1704	1361	1174
〃	〃	Nujol	1709	1370	1167
2-CH_3-5-$NO_2C_6H_3$	H	$CHCl_3$	1733	1358	1163
〃	〃	Nujol	1712	1355	1172
〃	CH_3	$CHCl_3$	1709	1358	1166
〃	〃	Nujol	1724 1704	1359	1185
$CH_3SO_2N(p\text{-}C_6H_4CH_3)COC_6H_5$		$CHCl_3$	1689	1366	1166
〃		Nujol	1692 1675	1361	1170

phenomena, had their S-N stretching frequencies at much longer wave length region in solid state than in solution, as discussed later.

SO_2 Stretching and S-N Stretching Frequencies

Both asymmetric and symmetric mode of SO_2 stretching frequencies of N-acyl- and N-acyl-N-substituted-sulfonamide derivatives were compared with each other in each state and shown in Table I. Tertiary sulfonamides had both frequencies at shorter wave length region than secondary sulfonamides, and this observation confirmed the tendency conjectured Baxter, *et al.*'s data.[8]

N-Acetyl-N-methylsulfonamide derivatives measured in a solution of chloroform, carbontetrachloride, bromoform or carbondisulfide and in liquid state showed strong absorption bands at about 910 cm^{-1} as shown in Table II. These absorption bands might be assigned to S-N stretching vibration. It is important to note that seven compounds in the table which had splitted carbonyl absorptions showed a characteristic frequency shift of about 50~60 cm^{-1} of the band to a longer wave length region in solid state. Presumably, the splitting phenomenon of carbonyl absorption and the frequency shift of S-N stretching vibration may originate from the same reason.

Table II. Absorptions of N-Acetyl-N-methyl-alkyl (or benzene)-sulfonamide Derivatives at 900 cm^{-1} Region

R	$RSO_2N(CH_3)COCH_3$ Measured in						
	Nujol	Liquid	$CHCl_3$	Δ (cm^{-1})	CS_2	$CHBr_3$	CCl_4
CH_3	855		912	57	909	912	911
C_2H_5	852		912	60	909	910	911
p-$CH_3C_6H_4$	861		908	47	907	—	—
m-$NO_2C_6H_4$	851		909	58	905	908	—
2-CH_3-5-$NO_2C_6H_3$	856		907	51	—	—	—
α-$C_{10}H_7$	851		907	56	905	—	—
p-CNC_6H_4	858		—	—	—	—	—
β-$C_{10}H_7$	911		907	−4	906	908	—
C_6H_5		907	910	3	905	—	—
p-ClC_6H_4		907	907	0	909	—	—
o-$CH_3C_6H_4$		906	908	2	908	908	—
p-$CH_3OC_6H_4$		907	909	2	905	—	—

Δ(cm^{-1}): (wave numbers in $CHCl_3$)-(wave numbers in Nujol mull or liquid film)

C-N Stretching Frequencies

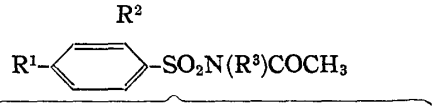
N-Acetyl-N-alkylmethane(or ethane)sulfonamide derivatives absorbed strongly at about 1125 cm^{-1} region as shown in Table III. N-Acetyl-N-alkyl-phenylsulfonamide derivatives also showed absorption bands at the same wave length region, which were generally weak. Since N-acetyl-N-arylsulfonamide derivatives showed no comparable band at this region, these absorption bands might be connected with the partial structure, N-acetyl-N-alkyl, of the molecule. Then the probable assignment was assumed to be C-N stretching mode of the group N-CH_2R. The observation of Katritzky, *et al.*,[9] in which N-aryl-N-methyl-methanesulfonamide and N-aryl-N-methylacetamide had their C-N stretching mode of vibrations at 1062~1076 cm^{-1} and 1140~1000 cm^{-1}, respectively, might confirm the above assumption.

8) J.N. Baxter, J. Cymerman-Craig, J.B. Willis: J. Chem. Soc., **1955**, 669.
9) A.R. Katritzky, R.A. Jones: *Ibid.*, **1960**, 4497.

C-CO-N Asymmetric Stretching Frequencies

N-Acyl-N-substituted-sulfonamide derivatives showed very strong absorption bands in the region of 1250~1290 cm^{-1} as shown in Table IV. This absorption bands might be assigned to an asymmetric stretching mode of the C-CO-N group by the analogy of an asymmetric stretching mode of the C-CO-R group in N,N-dimethylbenzamide.[10]

TABLE III. Absorptions of N-Acetyl-N-alkylsulfonamide Derivatives at 1125 cm^{-1} Region

$R^1SO_2N(R^2)COCH_3$								
R^1	R^2	cm^{-1}		R^1	R^2	R^3	cm^{-1}	
CH_3	CH_3	1124	S	H	H	CH_3	1125	W
〃	C_2H_5	1124	〃	CH_3O	〃	〃	1116	〃
〃	C_3H_7	1126	〃	Cl	〃	〃	1125	〃
〃	C_4H_9	1126	〃	H	CH_3	〃	1122	〃
〃	C_6H_{11}	1155	〃	〃	〃	C_2H_5	1122	〃
C_2H_5	CH_3	1125	〃	〃	〃	C_3H_7	1121	〃
〃	C_2H_5	1122	〃	〃	〃	C_4H_9	1126	〃

S: strong band W: weak band

Experimental

Syntheses of Samples*4

N-Acetyl-N-methylmethanesulfonamide——N-Methylmethanesulfonamide was refluxed with Ac_2O for 2 hr. After removal of the solvent *in vacuo*, the remained crystals were recrystallized from EtOH to colorless leaflets, m.p. 76°. *Anal.* Calcd. for $C_4H_9O_3NS$: C, 31.78; H, 6.00; N, 9.27. Found: C, 31.38; H, 5.97; N, 8.91.

N-Acetyl-N-methylethanesulfonamide——Prepared from N-methylethanesulfonamide similarly as above. Recrystallization from EtOH gave colorless prisms, m.p. 72°. *Anal.* Calcd. for $C_5H_{11}O_3NS$: C, 36.35; H, 6.71; N, 8.48. Found: C, 36.25; H, 6.48; N, 8.03.

N-Acetyl-N-methyl-2-methyl-5-nitrobenzenesulfonamide——To a solution of N-acetyl-2-methyl-5-nitrobenzenesulfonamide in EtOH an ethereal solution of CH_2N_2 was added, and the mixture was allowed to stand at room temperature overnight. After removal of the solvent the crystalline residue was recrystallized from aq. EtOH. Pale yellow needles, m.p. 132~133°. *Anal.* Calcd. for $C_{10}H_{12}O_5N_2S$: C, 44.11; H, 4.44; N, 10.29. Found: C, 44.00; H, 4.47; N, 10.11.

N-Acetyl-N-methyl-4-cyanobenzenesulfonamide——Prepared from N-acetyl-4-cyano-benzenesulfonamide similarly as above. Recrystallization from aq. EtOH gave colorless prisms, m.p. 101~102°. *Anal.* Calcd. for $C_{10}H_{10}O_3N_2S$: N, 11.76. Found: N, 11.56.

N-Acetyl-N-methylbenzenesulfonamide——To a solution of N-acetylbenzenesulfonamide in EtOH, an ethereal solution of CH_2N_2 was added, and the mixture was allowed to stand at room temperature overnight. After removal of the solvent, the oily residue was purified by distillation under reduced pressure. Colorless liquid, b.p_6 ca. 140°(bath temp.). *Anal.* Calcd. for $C_9H_{11}O_3NS$: N, 6.57. Found: N, 6.46.

N-Acetyl-N-methyl-4-chlorobenzenesulfonamide——Prepared from N-acetyl-4-chlorobenzenesulfonamide similarly as above. Colorless liquid, b.p_6 ca. 150° (bath temp.). *Anal.* Calcd. for $C_9H_{10}O_3NSCl$: N, 5.65. Found: N, 5.83.

N-Acetyl-N-methyl-4-methoxybenzenesulfonamide——Prepared from N-acetyl-4-methoxybenzenesulfonamide similarly as above. Colorless liquid, b.p_6 ca. 160°(bath temp.). *Anal.* Calcd. for $C_{10}H_{13}O_4NS$: N, 5.76. Found: N, 5.49.

N-Propylmethanesulfonamide——Methanesulfonyl chloride was added to a solution of propylamine in pyridine, and mixture was allowed to stand at room temperature for several hr. The reaction mixture was acidified with dil. HCl, extracted with AcOEt, and the AcOEt layer was washed with H_2O.

*4 All melting points were uncorrected.

10) S. Pinchas, *et al.*: J. Chem. Soc., **1961**, 3063.

Table IV. Absorptions of Tertiary Sulfonamide Derivatives at ca. 1250～1290 cm^{-1} Region

$R^1SO_2N(R^2)COR^3$				
R^1	R^2	R^3		cm^{-1}
CH_3	CH_3	CH_3	Nujol	1294
〃	〃	〃	CS_2	1259
〃	C_2H_5	〃	liquid	1259
〃	〃	〃	CS_2	1253
〃	C_3H_7	〃	liquid	1295
〃	C_4H_9	〃	〃	1253
〃	C_6H_5	〃	Nujol	1258
〃	〃	〃	CS_2	1274
〃	*p*-$C_6H_4CH_3$	〃	Nujol	1284
C_2H_5	CH_3	〃	〃	1285
〃	〃	〃	CS_2	1259
〃	C_2H_5	〃	liquid	1253
〃	〃	〃	CS_2	1250
p-$CH_3C_6H_4$	CH_3	〃	Nujol	1280
〃	〃	〃	CS_2	1261
〃	C_2H_5	〃	Nujol	1250
〃	〃	〃	CS_2	1252
〃	C_3H_7	〃	Nujol	1253
〃	C_4H_9	〃	〃	1264
〃	C_6H_{11}	〃	〃	1244
〃	C_6H_5	〃	〃	1276
〃	*p*-$C_6H_4CH_3$	〃	〃	1288
p-CNC_6H_4	CH_3	〃	〃	1267
p-ClC_6H_4	〃	〃	liquid	1282
〃	〃	〃	CS_2	1255
p-$CH_3OC_6H_4$	〃	〃	liquid	1267
〃	〃	〃	CS_2	1266
C_6H_5	〃	〃	liquid	1297
o-$CH_3C_6H_4$	〃	〃	〃	1290
〃	〃	〃	CS_2	1258
〃	C_2H_5	〃	liquid	1252
〃	〃	〃	CS_2	1248
〃	C_3H_7	〃	liquid	1244
〃	C_4H_9	〃	〃	1255
〃	C_6H_5	〃	Nujol	1266
〃	*p*-$C_6H_4CH_3$	〃	〃	1287
m-$NO_2C_6H_4$	CH_3	〃	〃	1284
〃	〃	〃	CS_2	1248
〃	C_2H_5	〃	Nujol	1256
〃	〃	〃	CS_2	1238
〃	C_3H_7	〃	Nujol	1292
〃	C_4H_9	〃	〃	1256
〃	C_6H_5	〃	〃	1277
2-CH_3-5$NO_2C_6H_3$	CH_3	〃	〃	1292
CH_3	C_6H_5	C_6H_5	〃	1292
〃	*m*-$C_6H_4CH_3$	〃	〃	1290
〃	*p*-$C_6H_4CH_3$	〃	CS_2	1263
C_2H_5	CH_3	〃	Nujol	1290
〃	〃	〃	CS_2	1288
〃	*m*-$C_6H_4CH_3$	〃	Nujol	1276
〃	*p*-$C_6H_4CH_3$	〃	〃	1279
p-$CH_3C_6H_4$	CH_3	〃	〃	1297

After removal of the solvent the crystalline residue was recrystallized from EtOH. Colorless needles, m.p. 29~30°. *Anal.* Calcd. for $C_4H_{11}O_2NS$: C, 35.02; H, 8.08. Found: C, 35.08; H, 8.15.

N-Butylmethanesulfonamide——Prepared from methanesulfonyl chloride and butylamine similarly as above. After removal of the solvent, the oily residue was purified by distillation under reduced pressure. Colorless liquid, $b.p_{5.5}$ 128°. *Anal.* Calcd. for $C_5H_{13}O_2NS$: C, 39.71; H, 8.66; N, 9.26. Found: C, 39.63; H, 8.65; N, 9.02.

N-Cyclohexylmethanesulfonamide——Prepared from methanesulfonyl chloride and cyclohexylamine similarly as N-propylmethanesulfonamide. Recrystallization from EtOH gave colorless prisms, m.p. 106°. *Anal.* Calcd. for $C_7H_{15}O_2NS$: C, 47.43; H, 8.53; N, 7.90. Found: C, 47.70; H, 8.52; N, 8.13.

N-*p*-Tolyl-*o*-toluenesulfonamide——Prepared from *o*-toluenesulfonyl chloride and *p*-toluidine similarly as above. Recrystallization from EtOH gave colorless prisms, m.p. 126°. *Anal.* Calcd. for $C_{14}H_{15}O_2NS$: C, 64.34; H, 5.79; N, 5.36. Found: C, 64.29; H, 6.00; N, 5.43.

N-Propyl-*o*-toluenesulfonamide——Prepared from *o*-toluenesulfonyl chloride and propylamine similarly as N-butylmethanesulfonamide. Colorless liquid, $b.p_7$ 173°. *Anal.* Calcd. for $C_{10}H_{15}O_2NS$: C, 56.31; H, 7.09; N, 6.57. Found: C, 56.04; H, 7.18; N, 6.46.

N-Acetyl-N-ethylmethanesulfonamide——N-Ethylmethanesulfonamide was acetylated with Ac_2O in the presence of anhyd. AcONa by refluxing for 5 hr. After cooling, the reaction mixture was poured into H_2O, and the mixture was extracted with AcOEt. The solvent was evaporated and the residue was distillated under reduced pressure. Colorless liquid, $b.p_{6.5}$ 105°. *Anal.* Calcd. for $C_5H_{11}O_3NS$: C, 36.35; H, 6.71; N, 8.48. Found: C, 35.74; H, 6.83; N, 8.23.

N-Acetyl-N-propylmethanesulfonamide——Prepared from N-propyl-methanesulfonamide similarly as above. Colorless liquid, $b.p_{5.5}$ 103°. *Anal.* Calcd. for $C_6H_{13}O_3NS$: C, 40.21; H, 7.31; N, 7.82. Found: C, 39.91; H, 7.38; N, 7.78.

N-Acetyl-N-butylmethanesulfonamide——Prepared from N-butylmethanesulfonamide similarly as above. Colorless liquid, $b.p_{6.5}$ 117°. *Anal.* Calcd. for $C_7H_{15}O_3NS$: C, 43.50; H, 7.82; N, 7.25. Found: C, 43.55; H, 7.89; N, 7.21.

N-Acetyl-N-cyclohexylmethanesulfonamide——N-Cyclohexylmethanesulfonamide was acetylated with Ac_2O in the presence of anhyd. AcONa by refluxing for 20 hr. After cooling, the mixture was poured into H_2O, the separated crystals were collected by filtration, recrystallized from EtOH. Colorless prisms, m.p. 72°. *Anal.* Calcd. for $C_9H_{17}O_3NS$: C, 49.29; H, 7.81; N, 6.39. Found: C, 49.51; H, 7.87; N, 6.42.

N-Acetyl-N-phenylmethanesulfonamide——Prepared from N-phenylmethanesulfonamide similarly as above, by refluxing for 5 hr. Recrystallization from EtOH gave colorless needles, m.p. 123°. *Anal.* Calcd. for $C_9H_{11}O_3NS$: C, 50.69; H, 5.20; N, 6.57. Found: C, 50.76; H, 5.38; N, 6.65.

N-Acetyl-N-*p*-tolylmethanesulfonamide——Prepared from N-*p*-tolylmethanesulfonamide similarly as above. Recrystallization from EtOH gave colorless plates, m.p. 116°. *Anal.* Calcd. for $C_{10}H_{13}O_3NS$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.81; H, 5.82; N, 6.23.

N-Acetyl-N-ethylethanesulfonamide——Prepared from N-ethylethanesulfonamide similarly as N-acetyl-N-ethylmethanesulfonamide. Colorless liquid, $b.p_7$ 105°. *Anal.* Calcd. for $C_6H_{13}O_3NS$: C, 40.21; H, 7.31; N, 7.81. Found: C, 39.92; H, 7.29; N, 7.69.

N-Acetyl-N-methyl-*p*-toluenesulfonamide——Prepared from N-methyl-*p*-toluenesulfonamide similarly as N-acetyl-N-cyclohexylmethanesulfonamide. Recrystallization from EtOH gave colorless prisms, m.p. 54~55°. *Anal.* Calcd. for $C_{10}H_{13}O_3NS$: C, 52.85; H, 5.77; N, 6.16. Found: C, 52.86; H, 6.00; N, 5.68.

N-Acetyl-N-ethyl-*p*-toluenesulfonamide——Prepared from N-ethyl-*p*-toluenesulfonamide similarly as above. Recrystallization from EtOH gave colorless prisms, m.p. 58°. *Anal.* Calcd. for $C_{11}H_{15}O_3NS$: N, 5.80. Found: N, 5.72.

N-Acetyl-N-propyl-*p*-toluenesulfonamide——Prepared from N-propyl-*p*-toluenesulfonamide similarly as above. Recrystallization from EtOH gave colorless plates, m.p. 45°. *Anal.* Calcd. for $C_{12}H_{17}O_3NS$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.41; H, 6.75; N, 5.35.

N-Acetyl-N-cyclohexyl-*p*-toluenesulfonamide——Prepared from N-cyclohexyl-*p*-toluenesulfonamide similarly as above. Recrystallization from EtOH gave colorless needles, m.p. 81°. *Anal.* Calcd. for $C_{15}H_{21}O_3NS$: N, 4.74. Found: N, 4.73.

N-Acetyl-N-methyl-*o*-toluenesulfonamide——Prepared from N-methyl-*o*-toluenesulfonamide similarly as N-acetyl-N-ethylethanesulfonamide. Colorless liquid, $b.p_2$ 132°. *Anal.* Calcd. for $C_{10}H_{13}O_3NS$: N, 6.16. Found: N, 5.69.

N-Acetyl-N-ethyl-*o*-toluenesulfonamide——Prepared from N-ethyl-*o*-toluenesulfonamide similarly as above. Colorless liquid, $b.p_{10}$ 167°. *Anal.* Calcd. for $C_{11}H_{15}O_3NS$: C, 54.75; H, 6.27; N, 5.80. Found: C, 54.50; H, 6.04; N, 5.86.

N-Acetyl-N-propyl-*o*-toluenesulfonamide——Prepared from N-propyl-*o*-toluenesulfonamide similarly as above. Colorless liquid, $b.p_6$ 158~159°. *Anal.* Calcd. for $C_{12}H_{17}O_3NS$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.35; H, 6.71; N, 5.43.

N-Acetyl-N-butyl-*o*-toluenesulfonamide——Prepared from N-butyl-*o*-toluenesulfonamide similarly as above. Colorless liquid, $b.p_5$ 146°. *Anal.* Calcd. for $C_{13}H_{19}O_3NS$: C, 57.97; H, 7.11; N, 5.20. Found: C, 57.78; H, 7.11; N, 5.14.

N-Acetyl-N-phenyl-*o*-toluenesulfonamide——Prepared from N-phenyl-*o*-toluenesulfonamide similarly as N-acetyl-N-cyclohexyl-*p*-toluenesulfonamide. Colorless needles, m.p. 100°. *Anal.* Calcd. for $C_{15}H_{15}O_3NS$: C, 62.26; H, 5.23; N, 4.74. Found: C, 62.14; H, 5.19; N, 4.84.

N-Acetyl-N-*p*-tolyl-*o*-toluenesulfonamide——Prepared from N-*p*-tolyl-*o*-toluenesulfonamide similarly as above. Colorless prisms, m.p. 155°. *Anal.* Calcd. for $C_{16}H_{17}O_3NS$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.53; H, 5.74; N, 5.57.

N-Acetyl-N-propyl-*m*-nitrobenzenesulfonamide——Prepared from N-propyl-*m*-nitro-benzenesulfonamide similarly as above. Pale yellow needles, m.p. 72°. *Anal.* Calcd. for $C_{11}H_{14}O_5N_2S$: C, 46.15; H, 4.93; N, 9.78. Found: C, 46.30; H, 4.99; N, 9.28.

N-Acetyl-N-butyl-*m*-nitrobenzenesulfonamide——Prepared from N-butyl-*m*-nitrobenzenesulfonamide similarly as above. Pale yellow needles, m.p. 83°. *Anal.* Calcd. for $C_{12}H_{16}O_5N_2S$: C, 47.99; H, 5.37; N, 9.33. Found: C, 48.22; H, 5.52; N, 9.32.

N-Acetyl-N-phenyl-*m*-nitrobenzenesulfonamide——Prepared from N-phenyl-*m*-nitrobenzenesulfonamide similarly as above. Pale yellow needles, m.p. 156°. *Anal.* Calcd. for $C_{14}H_{12}O_5N_2S$: C, 52.50; H, 3.78; N, 8.75. Found: C, 52.61; H, 3.91; N, 8.72.

N-Acetyl-N-methyl-α-naphthylsulfonamide——Prepared from N-methyl-α-naphthylsulfonamide similarly as above. Colorless prisms, m.p. 112°. *Anal.* Calcd. for $C_{13}H_{13}O_3NS$: N, 5.32. Found: N, 5.20.

N-Benzoyl-N-*m*-tolylmethanesulfonamide——A solution of N-*m*-tolylmethanesulfonamide in pyridine was refluxed with a small excess of benzoyl chloride. After cooling, the reaction mixture was neutrallized with dil. sulfuric acid and the precipitated crystals were collected by filtration. Recrytallization from EtOH gave colorless needles, m.p. 118°. *Anal.* Calcd. for $C_{15}H_{15}O_3NS$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.17; H, 5.32; N, 4.68.

N-Benzoyl-N-methylethanesulfonamide——Prepared from N-methylethanesulfonamide similarly as above. Colorless needles, m.p. 89°. *Anal.* Calcd. for $C_{10}H_{13}O_3NS$: N, 6.16. Found: N, 6.03.

N-Benzoyl-N-*m*-tolylethanesulfonamide——Prepared from N-*m*-tolylethanesulfonamide similarly as above. Colorless needles, m.p. 127°. *Anal.* Calcd. for $C_{16}H_{17}O_3NS$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.60; H, 5.66; N, 4.33.

Infrared Spectra

The infrared spectra were measured with a Koken Model DS-301 recording infrared spectrophotometer using NaCl prisms.

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Summary

The splitting phenomenon of the carbonyl absorptions and the shifts of S-N stretching vibrations to a longer wave length region of some N-acyl-N-substituted-sulfonamide derivatives measured in solid state were described. Tertiary sulfonamides had their SO_2 stretching vibrations at a shorter wave length region than secondary sulfonamides. N-Acetyl-N-alkylmethane(or ethane)sulfonamide showed strong C-N stretching vibrations of the group N-CH_2-R at about 1125 cm^{-1}. N-Acyl-N-substituted-sulfonamide derivatives had very strong asymmetric stretching vibrations of the group C-CO-N at 1250~1290 cm^{-1}. Synthesis of some sulfonamide derivatives is also described.

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