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The Migration of the Alkyl Groups of 6-Acetyl and 6-Methoxycarbonyl Derivatives of 2,3-Dimethyl-5-alkylbenzofurans*1

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The migration of the 5-alkyl groups of 2,3-dimethyl-5-alkyl-6-benzofuranyl methyl ketones by aluminum chloride was studied further, and an analogous migration was observed in the cases of methyl 2,3-dimethyl-5-alkyl-6-benzofurancarboxylates. The 5-ethyl-, 5-*n*-propyl-, and 5-isopropyl-ketones were converted to the corresponding carboxylic acids by the bromoform reaction and then, further, to the esters. The action of aluminum chloride on the 5-*n*-propyl-ketone and the esters in carbon disulfide at room temperature afforded the corresponding 4-alkyl-compounds as a result of the migration of the 5-alkyl groups to the 4-position, analogously to the way in which the 5-ethyl- and 5-isopropyl-ketones had afforded two 4-alkyl-ketones. The structures of the compounds were confirmed by converting both the ketones and the esters to the same carboxylic acids and from the data of their IR, UV and NMR spectra and gas chromatograms. It was found that the 5-alkyl groups were less likely to migrate in the cases of the esters than the corresponding alkyl groups in the cases of the ketones, while the *n*-propyl groups of the ketone and the ester were less likely to migrate than the other alkyl groups, and that the migration seemed to be intramolecular, as the *n*-propyl group was not isomerized to an isopropyl group during the migration.

It has previously been reported that the action of aluminum chloride on *o*-alkylphenyl methyl ketones at 100—170°C,[1,2] and in some cases at room temperature[2] also, caused the migration of the *o*-alkyl groups to the *m*-position; moreover, one of the present authors and others[3,4] have recently reported that 2,3-dimethyl-5-ethyl- and 5-isopropyl-6-benzofuranyl methyl ketones (**3**a and c) afforded the corresponding 4-alkyl-ketones (**4**a and c) by the analogous migration of the 5-alkyl group to the 4-position.

Now in the present experiments, the migration of the alkyl groups of the benzofuranyl ketones (**3**), especially that of the *n*-propyl-ketone (**3**b), was studied further, and an analogous migration was observed also in the cases of the related methyl 2,3-dimethyl-5-alkyl-6-benzofurancarboxylates (**7**a, b, and c).

2,3-Dimethyl-5-*n*-propyl-6-benzofuranyl methyl ketone (**3**b) was prepared much as in the cases of the 5-ethyl-[5] and 5-isopropyl-ketones[4] (**3**a and c) by the action of acetyl chloride and aluminum chloride or stannic chloride on 2,3-dimethyl-5-*n*-propylbenzofuran (**2**b), which had, in turn, been prepared by the cyclo-dehydration of 3-(*p*-*n*-propylphenoxy)-butanone (**1**b). The ketones (**3**a, b, and c) were converted to the corresponding carboxylic acids (**5**a,b, and c) by the bromoform reaction,[6] and then to the methyl esters (**7**a,b, and c).

The ketone (**3**b) and the esters (**7**a,b, and c) were treated with aluminum chloride in carbon disulfide at room temperature to afford the corresponding 4-alkyl-ketone (**4**b) and -esters (**8**a,b, and c) as a result of the migration of the 5-alkyl groups to the 4-position, just as the 5-ethyl- and 5-isopropyl-ketones (**3**a and c) afforded the 4-alkyl-ketones[3,4] (**4**a and c) (see Table 1). The products were purified by distillation and then by crystallization from petroleum ether, except for the ketone (**4**b), which was purified by chromatography on alumina, with benzene as the solvent. The yields of the esters (**8**a,b, and c) were poorer than those of the

*1 A major part of this paper was presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) G. Baddeley, *J. Chem. Soc.*, **1944**, 232; G. Baddeley and A. G. Pendleton, *ibid.*, **1952**, 807; G. Baddeley and S. Varma, *ibid.*, **1957**, 2727; M. Lukin and B. B. Carson, *J. Org. Chem.*, **23**, 1007 (1958).

2) G. Baddeley, G. Holt and W. Pickles, *J. Chem. Soc.*, **1952**, 4162.

3) Y. Kawase, M. Hubert-Habart, J.-P. Buisson and R. Royer, *Compt. Rend.*, **258**, 5007 (1964).

4) Y. Kawase, R. Royer, M. Hubert-Habart, A. Cheutin, L. René and J.-P. Buisson, *Bull. Soc. Chim. Fr.*, **1964**, 3131.

5) R. Royer, M. Hubert-Habart, L. René and A. Cheutin, *ibid.*, **1964**, 1259.

6) Y. Kawase and M. Takashima, This Bulletin, **40**, 1224 (1967).

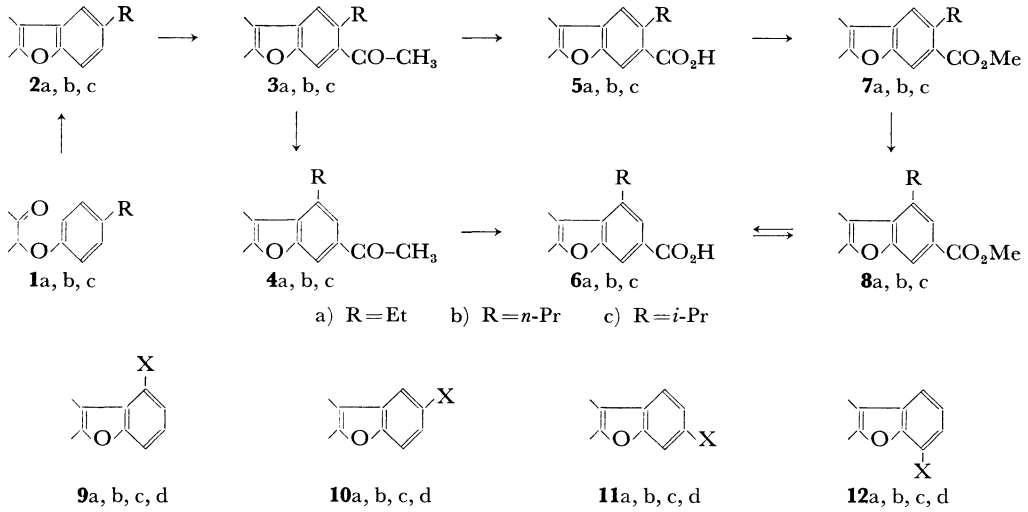

Chart 1

corresponding ketones (**4**a,b, and c), while those of the *n*-propyl-ketone (**4**b) and -ester (**8**b) were poorer than those of the other alkyl-compounds. The structures of the compounds were confirmed by converting both the ketones (**4**a,b, and c) and the esters (**8**a, b, and c) to the respective carboxylic acids (**6**a, b, and c) by bromoform reaction or hydrolysis; they were confirmed also by comparing their IR, UV, NMR, and gas chromatographical data with each other and with those of the compounds without *bz*-alkyl groups.

In the UV spectra, the absorption curves of the ketones (**3** and **4**), acids (**5** and **6**), and esters (**7** and **8**) are almost identical with each other and with those of the ketone (**11**b), acid (**11**c), and ester (**11**d) without the *bz*-alkyl group, except for a slight variation in the 210—230 mμ region according to the position of the *bz*-alkyl groups, and

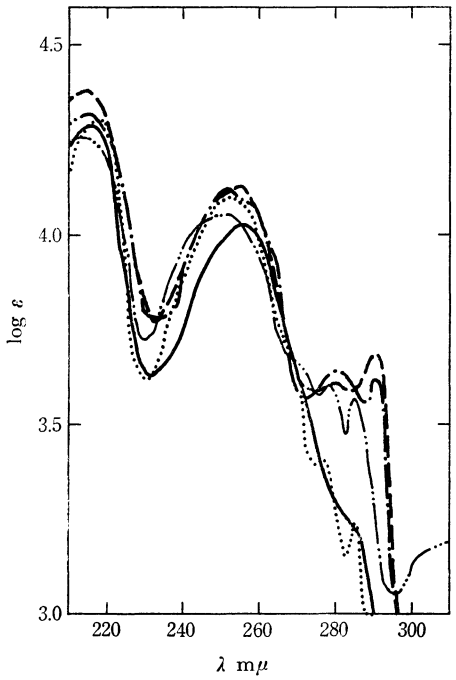

Fig. 1. The UV spectra of alkylbenzofurans. -·-· **2** (R=H), —— **9**a, ---- **10**a (=**2**a), -·-· **11**a, ···· **12**a

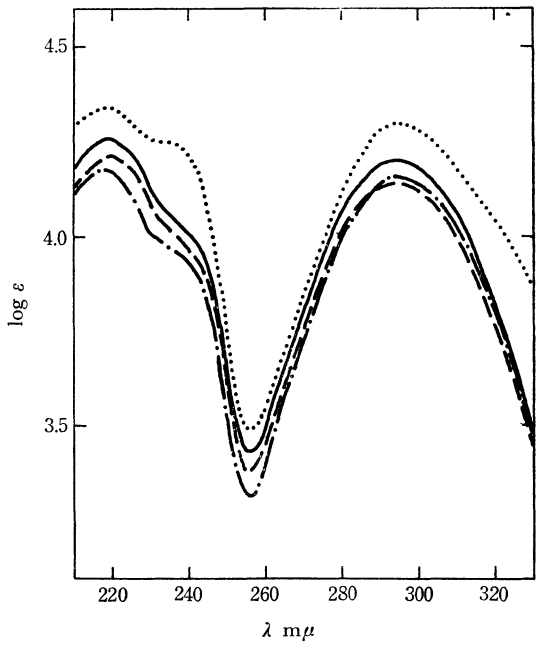

Fig. 2. The UV spectra of benzofuranyl ketones. -·-· **3** (R=Me), —— **3**a, ---- **3**b, ···· **3**c

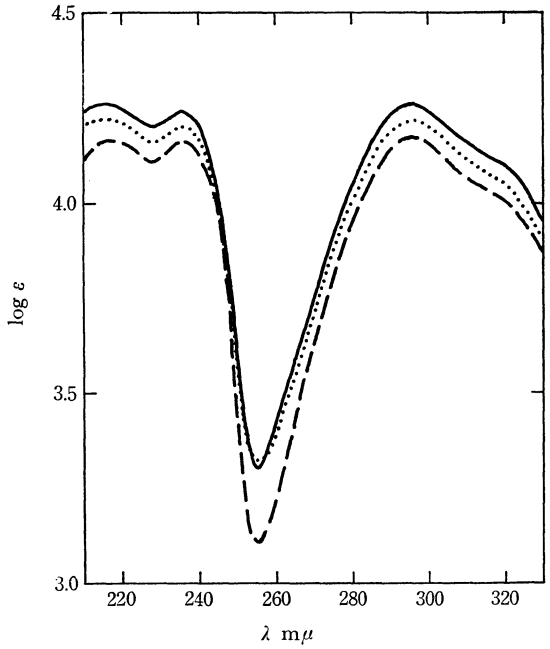

Fig. 3. The UV spectra of benzofuranyl ketones.
—— **4**a, ---- **4**b, ···· **4**c

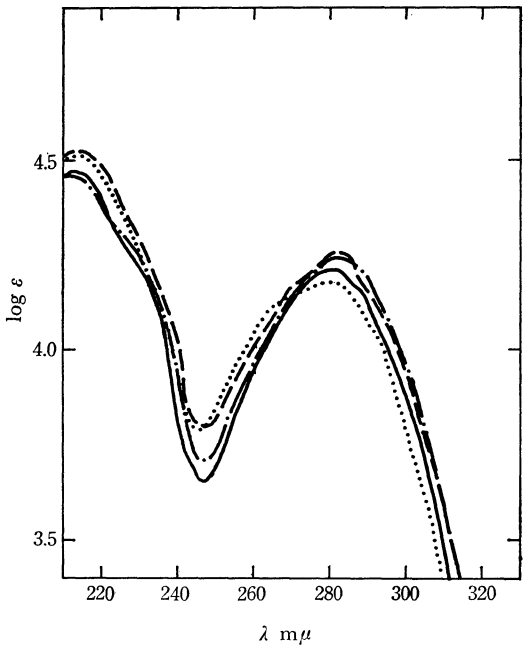

Fig. 5. The UV spectra of benzofurancarboxylic acids.
-·-· **5** (R=Me), —— **5**a, ---- **5**b, ····**5**c

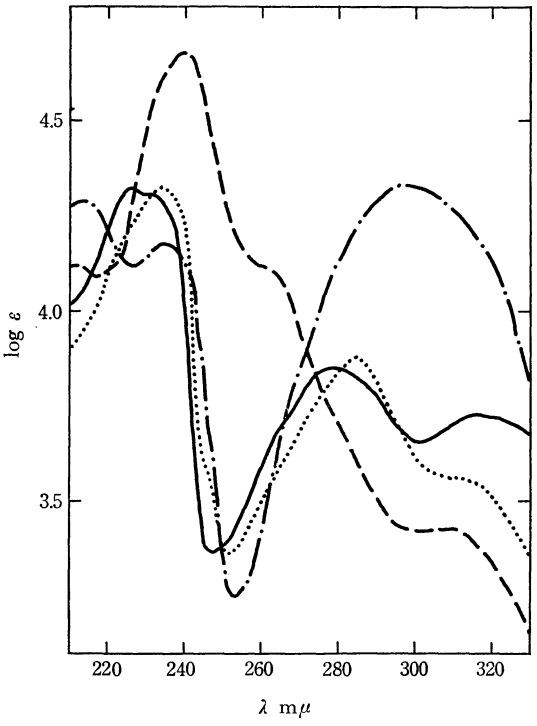

Fig. 4. The UV spectra of benzofuranyl ketones.
—— **9**b, ---- **10**b, -·-· **11**b, ···· **12**b

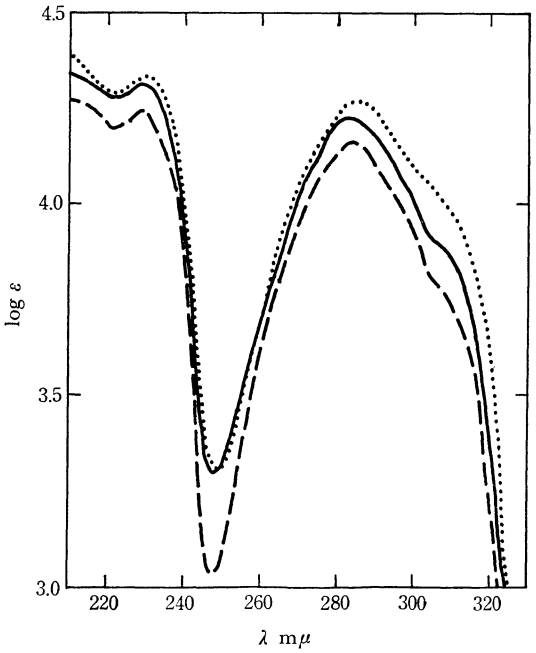

Fig. 6. The UV spectra of benzofurancarboxylic acids.
—— **6**a, ---- **6**b, ···· **6**c

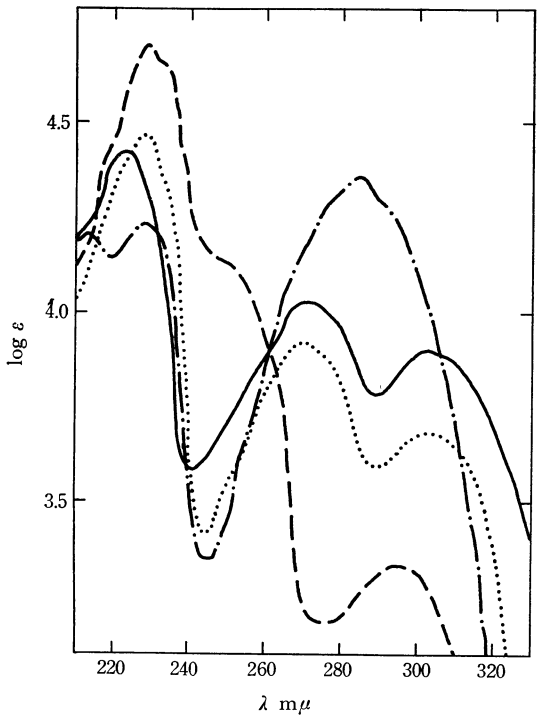

Fig. 7. The UV spectra of benzofurancarboxylic acids.
—— **9**c, ---- **10**c, -·-· **11**c, ···· **12**c

except for a slight shift of peaks by 1—5 mμ or 4—9 mμ in the cases of the esters and ketones, respectively, from those in the cases of the acids. Moreover, the absorption curves of the 6-acetyl-, 6-carboxyl-, and 6-methoxycarbonyl-2,3-dimethylbenzofurans (**11**b,c, and d) are quite different from those of the isomeric 4-, 5-, and 7-substituted compounds (**9**, **10**, and **12**); the absorption curves of the 4- and 7-isomers (**9** and **12**) are very similar to each other, having three peaks at 225—235 mμ, 270—285 mμ, and 300—315 mμ, while those of the 5-isomers (**10**) have remarkably high peaks at around 240 mμ, while those of the 6-isomers (**11**) have higher and broader peaks at 285—295 mμ (see the figures and Table 4).

In the NMR spectra, it was found that the peaks corresponding to the 3-methyl protons appeared at δ=2.04—2.14 ppm in the cases of the 5-alkyl-ketones and -esters (**3** and **7**), while they appeared at a field lower by about 0.13—0.26 ppm in the cases of the 4-alkyl-compounds (**4** and **8**); these differences are comparable to the cases of 2,3-dimethylbenzofurans substituted by electron-donating methoxyl, amino, ethyl, and chloro groups.[7] The peaks corresponding to the aromatic protons appeared as two singlets in the cases of **3**a,b, and c and **7**a,b, and c, while they appeared as two doublets (J=2 Hz) in the cases of **4**a,b, and c and **8**a,b, and c, indicating that the hydrogens are in the *para* and *meta* positions to each other respectively (see Table 5).

In the gas chromatograms, the peaks corresponding to the 4-alkyl-ketones (**4**) and -esters (**8**) appeared at 200—205°C, and those of the 5-alkyl-compounds (**3** and **7**) appeared at temperatures higher by about 5°C, while those of the 6-ketone and the 6-ester (**11**b and **11**d) appeared at 195 and 198°C respectively.

On the basis of these measurements, the ratio of the 5- and 4-alkyl-compounds (**3** and **4**, or **7** and **8**) in the crude rearrangement products of 5-alkyl-ketones or -esters (**3** or **7**) was determined by estimating the area of the peaks corresponding to the 5- and 4-alkyl-compounds in the gas chromatograms and that of the peaks corresponding to the 3-methyl protons of 5- and 4-alkyl-compounds in the NMR spectra (see Table 1). It seems that the 5-alkyl groups migrate less easily in the cases of the 5-alkyl-6-esters (**7**) than do the corresponding alkyl groups in the cases of the 5-alkyl-ketones (**3**), that the *n*-propyl group migrates less easily than the other alkyl groups, and that the migration is intramolecular, for the *n*-propyl group is not isomerized to an isopropyl group during the migration.

In conclusion, it seems that the migration of the 5-alkyl groups of 5-alkyl-6-ketones and -esters (**3** and **7**) by aluminum chloride occurs through the cationic cleavage of the alkyl group caused by the electron-attracting effect of the carbonyl group and by the steric hindrance of the aluminum chloride co-ordinated to the carbonyl group, followed by the synchronous attack of the split cationic alkyl group at the adjacent 4-position.

Experimental

All the boiling points and melting points are uncorrected. The IR spectra were measured in the form of KBr disks, the UV spectra were measured in an ethanol solution, the NMR spectra were measured on a Nihon Denshi 60 MHz spectrometer in a CCl_4 solution (5—10%), with TMS as the internal standard, and the gas chromatography was carried out on a Hitachi K23 apparatus, with Silicone DC-11 on Chamelite as the stationary phase, a flow rate of 46 ml/min (0.7 kg/cm²), and a temperature rise of 5°C/min from 180°C. The detailed data are summarized in the tables and figures.

Materials. a) Alkylbenzofurans. 2,3-Dimethylbenzofuran[8] (**2** R=H), 2,3,5-trimethylbenzofuran[5] (**2** R=Me), 2,3-dimethyl-5-ethyl-[8] and -5-isopropylbenzofurans[3,4] (**2**a and c) and 2,3-dimethyl-6- and -7-ethylbenzofurans[8] (**11**a and **12**a) were prepared following the methods in the respective references. 2,3-Dimethyl-5-*n*-propylbenzofuran (**2**b) and 2,3-dimethyl-4-ethylbenzofuran (**9**a) were prepared much as were **2**a and **11**a respectively.

7) Y. Kawase, *Chem. Ind.* (London), to be published.

8) E. Bisagni and R. Royer, *Bull. Soc. Chim. Fr.*, **1962**, 925.

TABLE 1. MIGRATION OF THE ALKYL GROUPS OF KETONES (**3**a, b, and c) AND ESTERS (**7**a, b, and c) BY $AlCl_3$ IN CS_2 AT ROOM TEMPERATURE

Starting compd.	Crude products: Bp °C/mmHg	Crude products: Yield %	Crude products: Composition[a]: Recovery %	Crude products: Composition[a]: Migrated %	Purified product,[b] Yield %
3a	186—193/17	75	10	90	**4**a, 60
3b	185—195/19	70	60	40	**4**b, 12[c]
3c	187—192/20	75	10	90	**4**c, 60
7a	187—191/19	75	40	60	**8**a, 17
7b	195—200/19	60	60	40	**8**b, 9
7c	186—192/21	90	10	90	**8**c, 40

a) The composition of the crude products were determined by gas chromatography and NMR spectra, and small amounts (about 1%) of the dealkylated compounds were detected in all cases by gas chromatography.
b) Crystallized from petroleum ether.
c) Purified by chromatography with alumina and benzene as a solvent furnishing also the 30% of recovery **3**b.

TABLE 2. RESULTS OF THE REACTIONS OTHER THAN THE MIGRATION

Starting compd.	Product	Method[a]	Yield %
b)	**1**b	A	79
1b	**2**b	B	74
2b	**3**b	C	48
2b	**3**b	D	46
3a	**5**a	E	78
3b	**5**b	E	80
3c	**5**c	E	62
4a	**6**a	E	74
4b	**6**b	E	67
4c	**6**c	E	83
5a	**7**a	F	78
5b	**7**b	F	77
5c	**7**c	F	67
6a	**8**a	F	69
8a	**6**a	G	62
8b	**6**b	G	70
8c	**6**c	G	55
9b	**9**a	H	51

a) A: 3-Chlorobutanone and K_2CO_3 in acetone, B: Cyclo-dehydration by H_2SO_4, C: Acetyl chloride and $AlCl_3$, D: Acetyl chloride and $SnCl_4$, E: Bromoform reaction, F: Esterification, G: Hydrolysis, and H: Reduction.
b) *p-n*-Propylphenol.

*3-(p-n-Propylphenoxy)butanone (**1**b).* Anhydrous potassium carbonate (98 g) was added to a solution of *p-n*-propylphenol (32 g) and 3-chlorobutanone (27.6 g) in acetone (200 m*l*), after which the mixture was refluxed for 9 hr. Most of the acetone was then distilled off, and the residue was dissolved in water and extracted with ether. The residual product obtained from the ethereal solution was distilled to give **1**b; bp 139—145°C/17 mmHg; 38.2 g (79%).

*2,3-Dimethyl-5-n-propylbenzofuran (**2**b).* Concentrated sulfuric acid (38 g) was stirred, drop by drop, into the butanone **1**b (38 g) with cooling below 30°C, and then the solution was allowed to stand at that temperature for 1 hr. The mixture was poured into ice water and extracted with ether. The ethereal solution was washed with an aqueous sodium hydroxide solution and dried, and then the ether was distilled off. The residual product from the ethereal solution was distilled to give **2**b; bp 138—140°C/18 mmHg; 25.7 g (74%).

*2,4-Dimethyl-4-ethylbenzofuran (**9**a).* A mixture of 2,3-dimethyl-4-benzofuranyl methyl ketone[6] (**9**b) (1.9 g), hydrazine hydrate (0.8 g), and diethylene glycol (30 m*l*) was heated gently for 1.5 hr in a distillation apparatus to distill off the water formed. Potassium hydroxide (2.9 g) was then gradually added to the slightly-cooled mixture in the same apparatus, and the mixture was heated gently for 1 hr to complete the development of nitrogen. The hot mixture was poured into water, acidified with dilute hydrochloric acid, and extracted with ether. After the ether was then distilled off, the residue was distilled to give **9**a; bp 127—131°C/17 mmHg; 0.9 g (51%).

b) Benzofuranyl Ketones. 2,3,5-Trimethyl-6-benzofuranyl methyl ketone[5] (**3** (R=Me)), 2,3-dimethyl-5-ethyl-[5] and -5-*i*-propyl-6-benzofuranyl methyl ketones[3,4] (**3**a and c) and 2,3-dimethyl-4-,[6] -5-,[9] -6-,[8] and -7-benzofuranyl methyl ketones[10] (**9**b, **10**b, **11**b, and **12**b) were prepared following the methods of the respective references. 2,3-Dimethyl-5-*n*-propyl-6-benzofuranyl methyl ketone (**3**b) was prepared much as were **3**a and c, as follows:

*2,3-Dimethyl-5-n-propyl-6-benzofuranyl Methyl Ketone (**3**b).*
i) By Aluminum Chloride. Powdered anhydrous aluminum chloride (15.4 g, 1.2 mol equivalents) was gradually added, with stirring and cooling, to a solution of the benzofuran **2**b (18 g) and acetyl chloride (8.3 g, 1.1 mol equivalents) in carbon disulfide (100 m*l*); the mixture was stirred at room temperature for 4 hr and then allowed to stand overnight. The mixture was poured into ice water and extracted with chloroform. The organic layer was washed with an aqueous sodium hydroxide solution and dried, and then the solvent was distilled off. The residual product was distilled, bp 187—200°C/22 mmHg, and then crystallized from petroleum ether to give **3**b; mp 45—47°C; 10.5 g (48%).

ii) By Stannic Chloride. Anhydrous stannic chloride (11.5 g, 1.5 mol equivalents) was gradually added, with stirring and cooling, to a solution of **2**b (5.5 g) and acetyl chloride (3 g, 1.3 mol equivalents) in carbon disulfide (50 m*l*); the mixture was then treated much as has been described in the case of aluminum chloride.

c) Benzofurancarboxylic Acids. 2,3,5-Trimethyl-6-benzofurancarboxylic acid[6] (**5** R=Me) and 2,3-dimethyl-4-,[6] -5-,[6] -6-,[6] and -7-benzofurancarboxylic

9) E. Bisagni, J.-P. Marquet, A. Cheutin, R. Royer and M. L. Desvoye, *Bull. Soc. Chim. Fr.*, **1965**, 1466.
10) C. Pène, P. Demerseman, A. Cheutin and R Royer, *ibid.*, **1966**, 586.

Table 3. The Mp, Bp, IR and analyses of the new compounds

Compd.	Mp °C (solv[a]) or bp °C/mmHg n (°C)	ν_{CO}^{KBr} cm^{-1}	Formula	Found C%	Found H%	Calcd C%	Calcd H%
			Aryloxybutanone				
1b	139—145/17 1.5030 (22)	1720	$C_{13}H_{18}O_2$	75.50	8.55	75.69	8.80
			Alkylbenzofurans				
2b	138—140/18 1.5360 (24)		$C_{13}H_{16}O$	82.85	8.77	82.93	8.57
9b	127—131/17 1.5512 (20.5)		$C_{12}H_{14}O$	82.61	8.05	82.72	8.10
			Benzofuranyl ketones				
3b	45—47[b] (P)	1680[c]	$C_{15}H_{18}O_2$	78.35	8.16	78.23	7.88
4b	44—45[d] (P)	1680[e]	$C_{15}H_{18}O_2$	78.08	8.06	78.23	7.88
			Benzofurancarboxylic acids				
5a	186—187.5 (E)	1685	$C_{13}H_{14}O_3$	71.12	6.50	71.54	6.47
5b	187—188 (E)	1685	$C_{14}H_{16}O_3$	72.19	7.16	72.39	6.94
5c	194—195.5 (E)	1685	$C_{14}H_{16}O_3$	72.50	7.39	72.39	6.94
6a	198—199 (E)	1670	$C_{13}H_{14}O_3$	71.25	6.48	71.54	6.47
6b	187—188 (E)	1670	$C_{14}H_{16}O_3$	71.99	7.08	72.39	6.94
6c	239—240 (E)	1670	$C_{14}H_{16}O_3$	71.98	6.74	72.39	6.94
			Methyl benzofurancarboxylates				
7a	177—180/20 1.5593 (22.5)	1710	$C_{14}H_{16}O_3$	72.11	7.08	72.39	6.94
7b	189—190/19 1.5572 (13)	1715	$C_{15}H_{18}O_3$	72.45	7.39	73.14	7.37
7c	182—184/20 1.5580 (9)	1725	$C_{15}H_{18}O_3$	72.91	7.47	73.14	7.37
8a	60—61.5 (P)	1710	$C_{14}H_{16}O_3$	72.55	7.06	72.39	6.94
8b	63—65 (P)	1710	$C_{15}H_{18}O_3$	73.22	7.52	73.14	7.37
8c	55—57 (P)	1710	$C_{15}H_{18}O_3$	73.22	7.60	73.14	7.37

a) E: Ethanol, P: Petroleum ether.
b) 2,4-Dinitrophenylhydrazone, mp 188—189°C (AcOEt). Found: C, 61.25; H, 5.15; N, 14.34%. Calcd for $C_{21}H_{22}O_5N_4$: C, 61.45; H, 5.40; N, 13.65%.
c) ν_{CO}^{KBr} of **3**a and **3**c are 1670 and 1685 cm^{-1}, respectively.
d) 2,4-Dinitrophenylhydrazone, mp 223—224°C (AcOEt). Found: C, 61.88; H, 5.41; N, 13.22%. Calcd for $C_{21}H_{22}O_5N_4$: C, 61.45; H, 5.40; N, 13.65%.
e) ν_{CO}^{KBr} of **4**a and **4**c are 1670 and 1680 cm^{-1}, respectively.

Table 4. The UV spectra

Compd.	λ_{max}^{EtOH} mμ[a]) (log ε)	Compd.	λ_{max}^{EtOH} mμ[a]) (log ε)
	Alkylbenzofurans	**5**c	215(4.51), 281(4.18)
2(R=H)	214(4.26), 251(4.05), 278(3.60), 285(3.56)	**6**a	229(4.31), 282(4.22)
9a	216(4.29), 256(4.03), 285[s](3.25)	**6**b	229(4.24), 284(4.16)
2a(=**10**a)	214(4.37), 254(4.13), 280(3.61), 291(3.69)	**6**c	230(4.23), 285(4.27)
11a	216(4.32), 252(4.12), 280(3.64), 291(3.62)	**9**c	224(4.42), 271(4.03), 304(3.90)
12a	218(4.30), 253(4.10), 276(3.41), 285(3.24)	**10**c	229(4.70), 252[s](4.10), 295(3.33)
	Benzofuranyl ketones	**11**c	212(4.22), 228(4.24), 285(4.35)
3(R=Me)	218(4.10), 240[s](3.48), 296(4.09)	**12**c	228(4.46), 270(3.92), 303(3.69)
3a	219.5(4.13), 240[s](4.01), 294(4.10)		**Methyl benzofurancarboxylates**
3b	220(4.11), 240[s](3.48), 294(4.07)	**7**(R=Me)	214(4.12), 230[s](4.06), 285(4.10)
3c	219(4.17), 235[s](4.13), 295(4.15)	**7**a	215.5(4.19), 230[s](4.13), 284(4.14)
4a	215.5(4.13), 235.5(4.10), 296(4.13)	**7**b	215(4.19), 230[s](4.15), 284(4.15)
4b	216(4.11), 236[s](3.49), 293(4.01)	**7**c	215(4.18), 230[s](4.10), 282(4.12)
4c	215(4.11), 236(4.10), 295(4.11)	**8**a	211(4.12), 229.5(4.13), 284.5(4.11)
9b	226(4.32), 232[s](4.30), 279(3.85), 316(3.73)	**8**b	212.5(4.13), 230(4.15), 284.5(4.13)
10b	213(4.13), 240(4.68), 261[s](4.12), 310(3.43)	**8**c	211(4.11), 229.5(4.13), 284(4.11)
11b	213(4.29), 235(4.18), 296(4.33)	**9**d	226(4.39), 274(3.94), 307(3.83)
12b	233(4.32), 285(3.88), 315[s](3.55)	**10**d	233(4.77), 254[s](4.11), 290(3.42), 301(3.40), 329[s](3.11)
	Benzofurancarboxylic acids	**11**d	229(4.26), 288(4.34)
5(R=Me)	211(4.46), 282(4.35)	**12**d	229(4.45), 275(3.92), 306(3.70)
5a	213(4.67), 281(4.18)		
5b	214(4.52), 282(4.23)		

a) s: Shoulder.

TABLE 5. THE NMR SPECTRA[a)]

Compd.	Ph-H		Ph-CH<	CO-Me or CO_2Me	2-Me	3-Me	Ph-C-CH<	Ph-C-C-Me
			Aklylbenzofurans					
2(R=H)					2.13	1.91		
2(R=Me)			2.40		2.31	2.08		
2a(=**10a**)			2.64(q)		2.25	2.02	1.26(t)	
2b			2.54(t)		2.28	2.07	1.57(m)	0.90(t)
2c			2.94(m)		2.26	2.06	1.28(d)	
9a			2.82(q)		2.17	2.12	1.20(t)	
11a			2.61(q)		2.17	1.94	1.19(t)	
12a			2.82(q)		2.27	2.03	1.29(t)	
			Benzofuranyl ketones					
3(R=Me)	7.50	6.96	2.50	2.47	2.32	2.05		
3a	7.56	7.09	2.94(q)	2.51	2.34	2.10	1.19(t)	
3b	7.64	7.14	2.90(t)	2.54	2.37	2.12	1.52(m)	0.98(t)
3c	7.46	7.36	3.72(m)	2.49	2.28	2.06	1.25(d)	
4a	7.57(d)	7.43(d)	2.91(q)	2.47	2.33	2.23	1.26(t)	
	J=2 Hz							
4b	7.68(d)	7.48(d)	2.88(t)	2.49	2.35	2.26	1.60(m)	1.00(t)
	J=2 Hz							
4c	7.65(d)	7.65(d)	3.57(m)	2.53	2.37	2.31	1.36(d)	
	J=1 Hz							
9b				2.49	2.27	2.11		
10b				2.55	2.39	2.18		
11b				2.50	2.37	2.14		
12b				2.68	2.37	2.12		
			Methyl benzofurancarboxylates					
7(R=Me)	7.82	7.01	2.58	3.82	2.30	2.02		
7a	7.80	7.09	3.03(q)	3.82	2.31	2.06	1.22(t)	
7b	7.75	7.01	2.95(t)	3.78	2.30	2.04	1.51(m)	0.96(t)
7c	7.66	7.31	3.91(m)	3.81	2.28	2.06	1.30(d)	
8a	7.70(d)	7.49(d)	2.90(q)	3.79	2.32	2.24	1.29(t)	
	J=2 Hz							
8b	7.68(d)	7.47(d)	2.85(t)	3.81	2.35	2.26	1.63(m)	1.01(t)
	J=2 Hz							
8c	7.63(d)	7.55(d)	3.63(m)	3.89	2.37	2.32	1.35(d)	
	J=2 Hz							
9d				3.85	2.32	2.21		
10d				3.89	2.35	2.18		
11d				3.79	2.30	2.00		
12d				3.89	2.36	2.06		

a) δ (ppm) values determined on a Nihon Denshi 60 MHz spectrometer in CCl_4 (5—10% solution) with TMS as the internal standard and (d)=doublet, (t)=triplet, (q)=quartet, and (m)=multiplet.

acids[11] (**9c**, **10c**, **11c**, and **12c**) were prepared following the methods of the respective references.

d) Methyl Benzofurancarboxylates. Methyl 2,3,5-Trimethyl-5-benzofurancarboxylate[6] (**7** R=Me) and methyl 2,3-dimethyl-4-,[11] -5-,[6] -6-,[6] and -7-benzofurancarboxylates[11] (**9d**, **10d**, **11d**, and **12d**) were prepared following the methods of the respective references.

Migration of the Alkyl Groups of the Ketones (3) and the Esters (7). Powdered anhydrous aluminum chloride (4.7 g, 2 mol equivalents) was gradually added, with stirring and cooling, to a solution of the ketone **3b** (4 g) in carbon disulfide (50 m*l*), after which the mixture was stirred for 4 hr at room temperature and then allowed to stand overnight. The mixture was

11) Y. Kawase, T. Okada and T. Miwa, to be published.

then poured into ice water and extracted with chloroform. The organic layer was washed with an aqueous sodium hydroxide solution and dried, and then the solvent was distilled off. The residual product was distilled to give the crude product; bp 185—195°C/19 mmHg; 2.8 g (70%). By the same procedure, the ketone **3**a and c and the esters **7**a, b, and c afforded the crude products; their compositions were determined by gas chromatography and by NMR spectroscopy. The crystallization of the crude products from petroleum ether furnished the pure crystalline products except in the case of **3**b. The crystallization in the case of **3**b furnished only the crystalline-recovery ketone (0.2 g); a part (0.5 g) of the residual oil was purified, by chromatography with alumina and benzene as a solvent, to give the recovery ketone (0.2 g) and the rearranged ketone **4**b; mp 44—45°C, 0.1 g (total 12%).

2,3-Dimethyl-5- and -4-alkyl-6-benzofurancarboxylic Acids (5a,b, and c and 6a,b, and c). *a) by the Bromoform Reaction of the Ketones (3a,b, and c and 4a, b, and c).* A solution of **3**a (8 g) in dioxane (50 m*l*) was added, with cooling and stirring, to an aqueous sodium hypobromide solution, which had been prepared by adding bromine (23 g, 3.8 mol equivalents) with cooling to a mixture of sodium hydroxide (14.5 g, 9 mol equivalents), water (45 m*l*), and ice (45 g). Stirring was continued for 30 min and then for another 1.5 hr at 45°C. The cooled mixture was diluted with water and washed with ether, and the aqueous layer was acidified after the addition of a small amount of sodium bisulfite. The crystalline precipitates thus formed were collected and recrystallized from ethanol to give 2,3-dimethyl-5-ethyl-6-benzofurancarboxylic acid (**5**a); mp 186—187.5°C; 6.3 g (78%).

2,3-Dimethyl-5-*n*-propyl- and -5-isopropyl-6-benzofurancarboxylic acids (**5**b and c) and 2,3-dimethyl-4-ethyl-, -4-*n*-propyl- and -4-isopropyl-6-benzofurancarboxylic acids (**6**a,b, and c) were also obtained by this procedure.

b) By the Hydrolysis of the Esters (8a, b, and c). An aqueous potassium hydroxide solution (1 g in 4 m*l* of water) was added to a solution of **8**a (1 g) in ethanol (5 m*l*), and then the mixture was refluxed for 3 hr. The cooled solution was diluted with water, washed with ether, and then acidified to give the crystalline product (**6**a), which was then recrystallized from ethanol; mp 198—199°C; 0.6 g (62%).

2,3-Dimethyl-4-*n*-propyl- and -4-isopropyl-6-benzofurancarboxylic acid (**6**b and c) were also obtained by this procedure.

Methyl 2,3-Dimethyl-5- and -4-alkyl-6-benzofurancarboxylates (7a,b, and c and 8a). Powdered potassium carbonate (43 g, 6 mol equivalents) was added to a solution of **5**a (11.3 g) and dimethyl sulfate (13.2 g, 2 mol equivalents) in acetone (200 m*l*), after which the mixture was refluxed for 8 hr. Most of the acetone was distilled off, and the residue was treated with water and extracted with ether. The ethereal layer was washed with a dilute aqueous sodium hyroxide solution, and then the ether was distilled off. The residual product was distilled to give methyl 2,3-dimethyl-5-ethyl-6-benzofurancarboxylate (**7**a); bp 177—180°C/20 mmHg; 9.4 g (78%).

Methyl 2,3-dimethyl-5-*n*-propyl- and -5-isopropyl-6-benzofurancarboxylates (**7**b and c) and methyl 2,3-dimethyl-4-ethyl-6-benzofurancarboxylate (**8**a) were also obtained by this procedure.

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This paper is dedicated to Emeritus Professor Munio Katake in Commemoration of the 75th birthday, november, 30, 1969.