The Elimination of Carbon Monoxide from Acid Derivatives. Part III.[1] Planar Carbonium Ions as Necessary Intermediates

By **David G. Pratt** and **Eugene Rothstein,*** The University, Leeds

Elimination of carbon monoxide from acid chlorides by the Friedel-Crafts reaction is precluded if the resulting carbonium ions are restricted to non-planar geometry by bicyclic or other structures with a rigid molecular framework. In such cases the normal ketones are obtained.

THE Friedel-Crafts elimination of carbon monoxide from acid chlorides has been envisaged[2] as a unimolecular decomposition of a first formed complex such as (I) to give, initially, a relatively stable carbonium ion complex (II). Similar complexes with antimony hexafluoride have been isolated and identified by Olah and his co-workers.[3] Decarbonylation is not, as a rule, dependent on the fate of the carbonium ion, which can yield aromatic derivatives, unsaturated compounds, or other products, the formation of which may be preceded by rearrangement.[1]

$$R_3C{\cdot}COCl + Al_2Cl_6 \longrightarrow \underset{\text{(I)}}{R_3C{\cdot}\overset{+}{C}O[Al_2Cl_7]^-} \longrightarrow$$

$$\underset{\text{(II)}}{R_3\overset{+}{C}[Al_2Cl_7]^-} + CO \longrightarrow \text{Products}$$

Classes of acid derivative which eliminate carbon monoxide according to the above scheme include aliphatic and aromatic tertiary acid chlorides,[2a] and also secondary aromatic acid chlorides, particularly when electron-releasing groups are attached to the aromatic nucleus.[4] The aim of this work was to ascertain whether all tertiary acid chlorides would undergo this reaction notwithstanding the possible intervention of high energy intermediates (II) such as, for example, carbonium ions situated at the bridgeheads of ' rigid ' polycyclic systems. For carbonium ions to attain a minimum potential energy, the attached groups must lie in a plane and must

---

[1] Part II, E. Rothstein and W. G. Schofield, *J. Chem. Soc.*, 1965, 4566.

[2] (*a*) E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1961; (*b*) M. E. Grundy, E. Rothstein, and Wei-Hwa Hsü, *ibid.*, 1956, 4561.

[3] G. A. Olah, W. S. Tolgysi, S. J. Kuhn, M. E. Moffit, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 1328.

[4] M. E. Grundy, Wei-Hwas Hsü, and E. Rothstein, *J. Chem. Soc.*, 1960, 372.

be disposed at an angle of 120° to one another; the impossibility of this occurring with bicyclic and similar compounds was advanced by Bartlett and Knox,[5] and by subsequent workers,[6] as a reason for the slow solvolysis of halogen situated at such bridgehead positions.

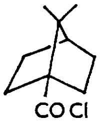
Decarbonylation of bridgehead acid chlorides should also be inhibited, because in these reactions the concentration of catalyst remains constant,[7] and there is, therefore, in some respects, an analogy with first-order unimolecular solvolysis of alkyl halides where concurrent bimolecular (S_N2) reactions are absent:

$$R_3C\cdot\overset{+}{C}O \longrightarrow R_3\overset{+}{C} + :CO$$

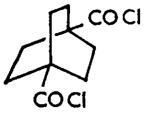
$$R_3C\cdot Cl \longrightarrow R_3\overset{+}{C} + :Cl^-$$

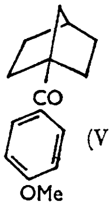
Deamination of cyclic bridgehead primary amines by nitrous acid or by nitrosyl chloride occurs, however, because formation of molecular nitrogen provides the driving force for the reaction.[8] As is apparent from the present work, this is not the case when carbon monoxide is eliminated.

We first examined the Friedel-Crafts reactions with apocamphane-1-carbonyl chloride (III), norbornane-1-carbonyl chloride (IV), and bicyclo[2,2,2]octane-1,4-dicarbonyl chloride (V) (Table 1; reactions 1, 2, and 3). None of these compounds evolved carbon monoxide but isolation of the 'normal' ketones showed that the initial complex (I) was formed, and hence the failure to eliminate carbon monoxide could be attributed to the high energy of the carbonium derivative (II). Steric hindrance, though not influencing decarbonylation, modified other reactions and is discussed later.


(III)


(IV)


(V)


(VI)

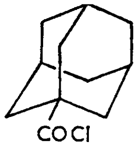
The negative results of the foregoing experiments were not inconsistent with the possibility that all chlorocarbonyl groups at bridgehead positions were stable; we therefore examined analogous reactions of adamantane-1-carbonyl chloride (VII), and of decalin-9-carbonyl chloride (VIII). These appeared to be suitable examples because both 1-chloroadamantane and 9-chlorodecalin undergo ready solvolysis in 80% ethanol.[6] As regards the former, Gleicher and Schleyer have suggested[9] that in spite of some similarities in their structures, there is a disparity between the reactivities of the adamantyl and bicyclo[2,2,2]octyl derivatives which is partly the consequence of the smaller non-bonding interactions of the 1-adamantyl cation in comparison with those of the corresponding cation of the bicyclo-compound.

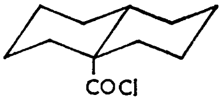
TABLE 1

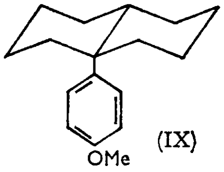
Friedel-Crafts reactions with bridgehead polycyclic acid chlorides, R·COCl

R	Solvent	CO (%)	Products
1 Apocamphane-1-	(*a*) Benzene [a]	0	None at room temperature. 1-Benzoylcamphane (25%) at the b.p.
	(*b*) Anisole	0	1-*p*-Methoxybenzoylapocamphane (VI) (75%)
	(*c*) Chloroform	0	No reaction
2 Norbornane-1-	(*a*) Benzene	0	1-Benzoylnorbornane (85%)
	(*b*) Chloroform	0	Soluble complex formed; no other reaction
3 Bicyclo[2,2,2]-octane-1,4-	(*a*) Benzene	0	1,4-Dibenzoylbicyclo-[2,2,2]octane
	(*b*) Chloroform	0	Insoluble complex formed; no other reaction
4 Adamantane-1-	(*a*) Benzene	56	1-Phenyladamantane (18%), and other products
	(*b*) Anisole	0	1-*p*-Methoxybenzoyladamantane (75%)
5 Decalin-9-	(*a*) Benzene	80	*trans*-Decalin (28%), phenyldecalin (16%)
	(*b*) Anisole	71	*trans*-9-Anisyldecalin (IX) (58%)

[a] Cf. also ref. 37.


(VII)


(VIII)


(IX)

The stability of the 9-decalyl carbonium ion, on the other hand, is fairly well established. It is considered to be an intermediate in both the Friedel-Crafts acetylation of decalin,[10] and the carboxylation of 2-decalol, which yields a mixture of *cis*- and *trans*-decalin-9-carboxylic acids.[11]

Carbon monoxide was eliminated from both the acid chlorides (VII) and (VIII). As might have been anticipated from its cage-like structure, the yield of gas from the first compound was appreciably smaller than that from the second (Table 1; experiments 4*a* and 5*a*). In benzene solution the major product from *trans*-decalin-9-carbonyl chloride (VIII) was *trans*-decalin and not the phenyl derivative (*trans*-9-phenyldecalin). In anisole, the reaction afforded *trans*-9-*p*-anisyldecalin (IX) and not *trans*-9-*p*-methoxybenzoyldecalin (Table 1; experiment 5*b*). Thus there were some unusual features of these reactions.

The formation of *trans*-decalin suggests a sterically hindered approach of the aromatic molecule to the

[5] P. D. Bartlett and L. H. Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184.

[6] Cf. R. C. Fort, jun. and P. von R. Schleyer, *Adv. Aliphatic Chem.*, 1966, **1**, 283.

[7] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1954.

[8] Ref. 6, p. 312 (cf. also p. 34 of the same volume).

[9] G. J. Gleicher and P. von Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 582.

[10] G. Baddeley and E. Wrench, *J. Chem. Soc.*, 1959, 1324.

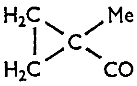
[11] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1959, **81**, 6332.

reaction centre, since a more reactive nucleophile (anisole) does yield the decalin derivative. Elimination of carbon monoxide from acid chlorides in anisole solution is unusual, but it occurs with 3-ethylpentane-3-carbonyl chloride [12] (10% yield), and predominantly with 2,2,3,5,5-pentamethylhexane-3-carbonyl chloride (X) which yields a *p*-anisyl derivative, the structure of which is probably (XI).[13]

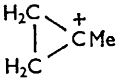
$$\underset{\text{(X)}}{\mathrm{CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}COCl}} \xrightarrow{\mathrm{PhOMe}} \underset{\text{(XI)}}{\mathrm{CMe_3{\cdot}CH_2{\cdot}CMe(CMe_3){\cdot}C_6H_4{\cdot}OMe}} + \mathrm{CO}$$

Although the high rate of decomposition of the compound (X) [12] is probably the principal reason for the almost exclusive formation of the *p*-anisyl derivative (XI), in other cases steric factors may be more important. This was indicated by the exceptional resistance of apocamphane-1-carbonyl chloride (III) to reaction with benzene (Table 1; reaction 1*a*) in comparison with the norbonyl derivative (IV) which is normal in this respect (Table 1; experiment 2*a*). The only difference between the two compounds is the *gem*-dimethyl group on the 7-position of the apocamphyl compound and it could be that that the aluminium tetrachloride ion was preferentially located on the side remote from this group, thus necessitating the approach of the aromatic molecule on the side where maximum steric hindrance could be expected. A combination of the two factors might have operated in the reactions of *trans*-decalin-9-carbonyl chloride.

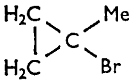
Among classes of acid chlorides which could be expected to resist decarbonylation are those derived from carbocyclic acids with small rings, because of the increased angular distortion of the corresponding carbonium ions, *e.g.* (XIII) and (XV). In fact, 1-methylcyclopropanecarbonyl chloride (XII) was not decomposed (Table 2; reaction 6*a*) and thus differed in reactivity from 1-methylcyclopropyl bromide (XIV), which undergoes slow solvolysis in aqueous ethanol at 130°.[14] On the other hand, 1-methylcyclobutanecarbonyl chloride afforded a moderate yield of carbon monoxide (Table 2; reaction 7*a*).



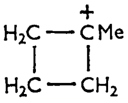
(XII)



(XIII)



(XIV)



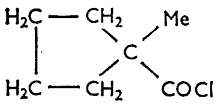
(XV)

1-Methylcyclopentanecarbonyl chloride (XVI) yielded 70% of carbon monoxide.[15] This is rather more than might have been expected, because in forming the carbonium ion (XVII) the cyclic angles are required to expand from near 109° to nearly 120°. It has, however, been suggested that the number of repulsions between neighbouring hydrogen atoms is reduced from ten to six in passing from a cyclopentane derivative [*e.g.* (XVI)] to the cyclopentyl ion [*e.g.* (XVII)], thus decreasing the relative energy of the transition state.[16]

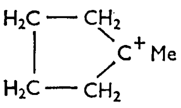
TABLE 2

Friedel-Crafts reactions with cyclic tertiary acid chlorides, R·COCl

	R	Solvent	CO (%)	Products
6	1-Methylcyclopropyl-	(*a*) Benzene	0	1-Benzoyl-1-methylcyclopropane + 50% recovered acid
		(*b*) Anisole	0	1-*p*-Methoxybenzoyl-1-methylcyclopropane (64%)
7	1-Methylcyclobutyl-	(*a*) Benzene	51	Unidentified ketones and other products
		(*b*) Anisole	0	1-*p*-Methoxybenzoyl-1-cyclobutane (70%)
8	1-Methylcyclopentyl-	(*a*) Benzene [14]	70	1-Methyl-1-phenylcyclopentane (67%)
		(*b*) Anisole [14]	0	1-*p*-Methoxybenzoyl-1-methylcyclopentane (61%)
9	*exo*-2-Methylnorbornyl-	(*a*) Benzene	85	Methylphenylnorbornane (?) (27%)
		(*b*) Anisole	0	2-*exo*-*p*-Methoxybenzoyl-2-methylnorbornane (84%)
10	*endo*-2-Methylnorbornyl	(*a*) Benzene	80	Identical with those of 9*a*
		(*b*) Anisole	0	2-*endo*-*p*-Methoxybenzoyl-2-methylnorborane (81%)

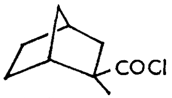


(XVI)

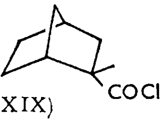


(XVII)

When the chlorocarbonyl groups were not attached to bridgehead carbon as in 2-methylnorbornane-2-*exo*- and 2-*endo*-carbonyl chlorides, (XVIII) and (XIX) respectively, *i.e.* when only two of the valency bonds of the carbon atom under consideration were rigidly fixed, decomposition was almost quantitative. There was little observable difference in reactivity between the *exo*- and the *endo*-isomers, which afforded identical mixtures of phenylated products (Table 2; reactions 9*a* and 10*a*). In anisole solution (Table 2; reactions 9*b* and 10*b*) the orientation of the bonds at C-2 was not altered and accordingly the *exo*- and the *endo*-acid chlorides yielded different *p*-anisyl ketones.



(XVIII)



(XIX)

---

[12] M. E. Grundy, Wei-Hwa Hsü, and E. Rothstein, *J. Chem. Soc.*, 1958, 581.

[13] W. Bleazard and E. Rothstein, *J. Chem. Soc.*, 1958, 3789.

[14] E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 2719.

[15] E. Rothstein and R. W. Saville, *J. Chem. Soc.*, 1949, 1950.

[16] J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, 1951, **73**, 5034; H. C. Brown and M. Borkowski, *ibid.*, 1952, **74**, 1895.

Secondary cyclic acid derivatives resembled those in the aliphatic series and did not liberate carbon monoxide under the usual conditions. In benzene solution, all the following compounds yielded nearly quantitative amounts of the corresponding phenyl ketones: norpinic anhydride,[17] norbornane-2-*endo*-carbonyl chloride, and as mentioned above, cyclobutanecarbonyl chloride. These compounds showed little tendency to decompose and were recovered virtually unchanged from their solutions in chloroform containing aluminium chloride.

EXPERIMENTAL

Reagents.—Purified thionyl chloride[18] was used for the preparation of the acid chlorides. Sodium-dried benzene (AnalaR) was used in the Friedel-Crafts reactions. Free-flowing 'purified' aluminium chloride was supplied by B. D. H. Ltd.

Acids and Acid Chlorides.—Apocamphane-1-carboxylic acid,[19] m.p. 215—219° (corr.) (lit.,[5] 217—218°) (Found: C, 71·5; H, 9·5. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·9%), $\nu_{max.}$ 1678 cm.$^{-1}$ (C=O). Acid chloride,[21] b.p. 76·5—77·0°/12 mm. (not previously recorded).

Norbornane-1-carboxylic acid, m.p. 110—111° (lit.,[20] 112—113°) (Found: C, 69·0; H, 8·7. Calc. for $C_8H_{12}O_2$: C, 68·6; H, 8·6%). Acid chloride,[21] b.p. 76·5—77·0°/12 mm. (not previously recorded).

Bicyclo[2,2,2]octane-1,4-dicarboxylic acid[22] (Found: C, 60·3; H, 7·3. Calc. for $C_{12}H_{18}O_4$: C, 63·7; H, 7·1%). Acid chloride, m.p. 96—98° [from light petroleum (b.p. 40—60°)] (lit.,[23] 97·5—98·5°).

Adamantane-1-carboxylic acid[24] gave adamantane-1-carbonyl chloride, b.p. 135—136°/10 mm. (not previously recorded), m.p. 51—53° [from light petroleum (b.p. 40—60°)] (lit.,[21] 48·5—52·0°).

trans-Decalin-9-carboxylic acid,[25,26] m.p. 132—134° (from aqueous ethanol) (lit.,[25] 134·5—135·5°) (Found: C, 72·6; H, 9·8. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 10·0%). Acid chloride, b.p. 118°/11 mm. (lit.,[26] 110—111°/8 mm.).

2-Methylnorborane-2-*exo*-carboxylic acid,[27] m.p. 50—52°, (lit.,[28] 52—53°) (Found: C, 70·2; H, 9·1. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·2%). Acid chloride, b.p. 88°/14 mm., (lit.,[28] b.p. 83°/12 mm.).

2-Methylnorbornane-2-*endo*-carboxylic acid,[27b, 29] m.p. 91—93°, (lit.,[28] m.p. 92—93°) (Found: C, 70·4; H, 9·1. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·2%). Acid chloride, b.p. 86°/14 mm. (lit.,[27a] 84°/12 mm.).

1-Methylcyclopropanecarboxylic acid, b.p. 110—112°/40 mm. (lit.,[30] 183—185°/1 atmos.), m.p. 32·5—34·0° (lit.,[31] 29·5—32·0°) (Found: C, 59·9; H, 8·4. Calc. for $C_5H_8O_2$: C, 60·0; H, 8·1%). Acid chloride, b.p. 128—129° (lit.,[32] 132—134°).

1-*Methylcyclobutanecarbonyl Chloride*.—(a) *Cyclobutyl phenyl ketone*. A much improved yield over those previously reported[33] was obtained by adding cyclobutanecarbonyl chloride[33] (82·9 g., 0·70 mole) during 75 min. to a stirred suspension of aluminium chloride (115 g., 0·86 mole) in benzene (200 c.c.). The solution was stirred for a further 4 hr. and then worked up in the usual way to give cyclobutyl phenyl ketone (101 g., 90%), b.p. 125°/11 mm. (lit.,[33] b.p. 122—125°/8 mm.). Freedom from by-products was shown by g.l.c. (polyethylene glycol at 180°). The ^{1}H n.m.r. (60 Mc./sec.) spectrum showed two groups of signals at τ 2·5—2·1 (Ph like those of cyclohexyl phenyl ketone)[34] others at 6·17 (irregular q, $CH_2{\cdot}\mathit{CH}{\cdot}CH_2$), and a group of 14 signals (6H) symmetrically centred at 7·78. There was a near correspondence with the spectrum of this compound reported by Applequist and McGreer,[35] but their chemical shift values were given in parts per hundred million from water with methylene dichloride as an external reference, and close comparisons could not be made.

(b) 1-*Methylcyclobutanecarboxamide*. Use of equivalent quantities of sodamide and cyclobutyl phenyl ketone[36] gave products which contained 50% of starting ketone (g.l.c.). The partially methylated material (76·7 g., 0·48 mole) was therefore boiled for 1 hr. under reflux with a suspension of freshly prepared sodamide (0·52 mole) in toluene (250 c.c.); the liquid was cooled, methyl iodide (350 g., 2·5 mole) was added, and then the mixture was boiled for a further 5 hr. G.l.c. showed only traces of impurities in the resulting 1-methylcyclobutyl phenyl ketone (51·4 g., 53%), b.p. 118—128°/12 mm. The group of signals in the ^{1}H n.m.r. spectrum at τ 6·17 corresponding to the tertiary proton had been replaced by a methyl peak at 8·45.

The methylated ketone (38·8 g., 0·223 mole) was boiled under reflux (5 hr.) with a finely powdered suspension of freshly prepared sodamide (0·465 mole) in anhydrous toluene (220 c.c.) to yield 1-methylcyclobutanecarboxamide (69%), m.p. 161—163° (from benzene), (lit.,[36] 165°).

(c) 1-*Methylcyclobutanecarboxylic acid and derivatives*. Incomplete decomposition resulted when the amide reacted with nitrous acid, and consequently it was boiled under reflux (2 hr.) with an excess (2 mol.) of 2N-sodium hydroxide, to yield, on acidification, 1-*methylcyclobutanecarboxylic acid* (93%), b.p. 98°/13 mm. (Found: C, 63·0; H, 8·8. $C_6H_{10}O_2$ requires C, 63·2; H, 8·9%). This gave (cold $SOCl_2$) the acid chloride (90%), b.p. 143—144°/772 mm., and thence the amide, m.p. 162—164° (from benzene). The *anilide* separated from light petroleum (b.p. 80—100°) as needles,

---

[17] Experiment by D. G. Fisher, Ph.D. Thesis, Leeds, 1961.

[18] D. L. Cottle, *J. Amer. Chem. Soc.*, 1946, **68**, 1380.

[19] D. N. Kursanov and S. V. Vitt, *Zhur. obschei Khim.*, 1955, **25**, 2509.

[20] H. Kwart and G. Null, *J. Amer. Chem. Soc.*, 1958, **80**, 248; 1959, **81**, 2765.

[21] P. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 2194.

[22] J. D. Roberts, W. T. Moreland, and W. Frazer, *J. Amer. Chem. Soc.*, 1953, **75**, 637.

[23] J. C. Kauer, R. E. Benson, and G. W. Parshall, *J. Org. Chem.*, 1965, **30**, 1431.

[24] H. Koch and W. Haaf, *Angew. Chem.*, 1960, **72**, 628.

[25] A. S. Hussey, H. D. Liao, and R. H. Barker, *J. Amer. Chem. Soc.*, 1953, **75**, 4727.

[26] W. G. Dauben, R. C. Tweit, and R. L. MacLean, *J. Amer. Chem. Soc.*, 1955, **77**, 48.

[27] (*a*) K. Alder, G. Stein, E. Rolland, and G. Schulz, *Annalen*, 1934, **514**, 197; (*b*) K. Alder and G. Schulz, *Chem. Ber.*, 1960, **93**, 809.

[28] S. Beckman, R. Scharber, and R. Bamburger, *Chem. Ber.*, 1954, **87**, 997.

[29] Ref. 28*a*, p. 211.

[30] M. Kohn and A. Mandelewitsch, *Monatsh.*, 1921, **42**, 227.

[31] S. Siegel and C. G. Bergstrom, *J. Amer. Chem. Soc.*, 1950, **72**, 3815.

[32] D. W. Hughes and J. C. Roberts, *J. Chem. Soc.*, 1960, 903.

[33] H. R. Henze and G. W. Gayler, *J. Amer. Chem. Soc.*, 1952, **74**, 3615.

[34] N.M.R. Spectra Catalog, Varian Associates, Palo Alto, California, 1963, no. 613.

[35] P. E. Applequist and D. E. McGreer, *J. Amer. Chem. Soc.*, 1960, **82**, 1965.

[36] K. E. Hamlin and U. Biermacher, *J. Amer. Chem. Soc.*, 1955, **77**, 6376.

m.p. 122—123° (Found: C, 76·4; H, 7·8; N, 7·6. $C_{12}H_{15}NO$ requires C, 76·2; H, 8·0; N, 7·4%).

Friedel-Crafts Reactions.—(a) *With apocamphane*-1-*carbonyl chloride*.

(i) *In benzene*. There was little or no reaction at room temp. No carbon monoxide was detected when a mixture of the acid chloride (4·82 g., 0·026 mole), aluminium chloride (4·1 g., 0·031 mole), and benzene (23 c.c.) was heated under reflux (2 hr.). The principal product (2·2 g.), b.p. 110—113°/0·04 mm., was (g.l.c. on silicone grease at 250°) a mixture (2 : 1) of two compounds: 1-benzoyl-7,7-dimethylnorbornane (1-benzoylapocamphane, m.p. 52—53·5° (needles from methanol) (lit.,[37] 49—50°), (Found: C, 84·3; H, 8·8. Calc. for $C_{16}H_{20}O_2$: C, 84·2; H, 8·9%), which was slowly deposited from the mixture; the residual oil did not crystallise and the second component was not isolated pure.

(ii) *In anisole*. The acid chloride (2·5 g., 0·013 mole) reacted at room temperature with a solution of aluminium chloride (2·2 g., 0·016 mole) in anisole (15 c.c.). The products were unchanged material (6%), and 1-p-*methoxybenzoylapocamphane* (2·6 g., 75%), b.p. 140°/0·04 mm., as needles, m.p. 81·5—82·5° [from light petroleum (b.p. 40—60°)] (Found: C, 79·3; H, 8·5. $C_{17}H_{22}O_2$ requires C, 79·0; H, 8·6%); *semicarbazone*, m.p. 167° (from dilute ethanol) (Found: C, 68·5; H, 8·1; N, 13·4. $C_{18}H_{25}N_3O_2$ requires C, 68·6; H, 8·0; N, 13·3%).

(iii) *In chloroform*. Experiment (ii) was repeated in chloroform solution. Carbon monoxide was not evolved and the starting material was recovered as the acid (94%).

(b) *With norbornane*-1-*carbonyl chloride*. (i) *In benzene*. The mixture of the acid chloride (2·5 g., 0·016 mole), aluminium chloride (2·4 g., 0·018 mole), and benzene (14 c.c.) afforded a clear homogeneous solution. Carbon monoxide was not liberated, and the product was 1-*benzoylnorbornane* (85%), b.p. 155—157°/9 mm., m.p. 35·5—36·0° [needles from light petroleum (b.p. 40—60°)] (Found: C, 84·1; H, 8·2. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%); *oxime* as long needles, m.p. 198—200° (corr.) (from 95% ethanol) (Found: C, 78·1; H, 8·0; N, 6·6. $C_{14}H_{17}NO$ requires C, 78·1; H, 8·0; N, 6·5%).

(ii) *In chloroform*. A similar mixture in chloroform gave a clear solution from which only norbornanecarboxylic acid (60%) was isolated.

(c) *With bicyclo*[2,2,2]*octane*-1,4-*dicarbonyl chloride*. (i) *In benzene*. An insoluble complex was formed when a solution of the acid chloride (1·25 g., 0·0053 mole) in benzene (3 c.c.) was slowly added to a stirred suspension of the catalyst (1·7 g., 0·013 mole) in benzene (10 c.c.). No gases were liberated and the mixture furnished 1,4-*dibenzoylbicyclo*[2,2,2]*octane*, m.p. 93—94° [from light petroleum (b.p. 100—120°)] (Found: C, 83·3; H, 7·1. $C_{22}H_{22}O_2$ requires C, 83·0; H, 7·0%).

(ii) *In chloroform*. Although a complex with the catalyst appeared to be formed, no reaction occurred and only the original acid was isolated (79%).

(d) *With adamantane*-1-*carbonyl chloride*. (i) *In benzene*.[38] The mixture of acid chloride (4·54 g., 0·0229 mole), aluminium chloride (3·48 g., 0·26 mole), and benzene (20 c.c.) yielded carbon monoxide (56%), and a little 1-phenyladamantane, identified by comparison of its i.r. spectrum with that published.[39]

(ii) *In anisole*. The product was 1-p-*methoxybenzoyladamantane* (75%), b.p. 180—185°/0·02 mm., which slowly crystallised and then separated from light petroleum (b.p. 40—60°) in large prisms, m.p. 66—67° (Found: C, 80·0; H, 8·1. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·2%); *oxime*, m.p. 233° (decomp.) (needles from aqueous dioxan) (Found: C, 75·9; H, 8·2; N, 4·8. $C_{18}H_{23}NO_2$ requires C, 75·8; H, 8·2; N, 4·9%).

(e) *With* trans-*decalin*-9-*carbonyl chloride*. (i) *In benzene*.* The reaction yielded carbon monoxide (80%) and *trans*-decalin (28%), b.p. 58°/10 mm. (Found: C, 86·8; H, 13·1. Calc. for $C_{10}H_{18}$: C, 87·0; H, 13·0%), i.r. spectrum identical with that published.[40] There were no olefinic absorptions. A second fraction (16%), b.p. 131·5°/0·2 mm., (lit.,[10] 158—164°/15 mm.) was, according to Baddeley and Wrench [10] a phenyldecalin, although the b.p. was too high to be that of either *cis*- or *trans*-9-phenyldecalin (b.p. 97—98°/0·3 mm.[41]) (Found: C, 89·8; H, 9·7. Calc. for $C_{16}H_{22}$: C, 89·9; H, 10·3%).

(ii) *In anisole*. Carbon monoxide (71%) was evolved. Decalin was not obtained but there was a small amount of material, b.p. 95—96°/7 mm. which contained halogen and had the correct analysis for a chlorodecalin (*trans*-9-chlorodecalin has b.p. 83°/7 mm.[42]) (Found: C, 70·3; H, 10·0. Calc. for $C_{10}H_{17}Cl$: C, 69·5; H, 9·9%). The principal product was a liquid, b.p. 135—140°/0·15 mm. which soon deposited 9-p-*anisyl*-trans-*decalin* (43%), m.p. 76—76·5° [from light petroleum (b.p. 40—60°)] (Found: C, 83·2; H, 9·8. $C_{17}H_{24}O$ requires C, 83·6; H, 9·9%). A weak carbonyl absorption at 1695 cm.$^{-1}$ in the spectrum of the liquid was not shown by the recrystallised specimen.

The following considerations led to the formulation of the anisyl derivative. When α- and β- (as well as 9-) decalols are treated with a mixture of sulphuric and formic acids, the products are *cis*- and *trans*-decalin-9-carboxylic acids, *i.e.*, the 9-carbonium ion is the result of any rearrangement.[43] The ^1H n.m.r. spectrum shows a broad band (16H) with centre at τ 8·49, characteristic of *trans*-decalin derivatives.[43,44] Some indication of the angular proton between 7·4 and 7·6 was observed, but the resolution was too poor for any certainty in this respect, though this is the region where such signals could be expected. Finally absorptions at 1·8 and 2·2 (4 aromatic H, AB structure, *J* 8·5 c./sec.), and at 6·3 (s, OMe) corresponded to the anisyl group.

(f) *With* 1-*methylcyclopropanecarbonyl chloride*. (i) *In benzene*. A mixture in benzene (36 c.c.) of the acid chloride (4·87 g., 0·041 mole) and aluminium chloride (6·01 g., 0·045 mole) was stirred at room temperature for 3 hr. No carbon monoxide was liberated. The mixture afforded 1-methylcyclopropanecarboxylic acid (2·15 g., 52%) and two neutral liquids, b.p. 115—130°/8 mm. 120—140°/0·03 mm. of which only the first was examined. G.l.c. (polyethylene glycol at 170°) and its i.r. spectrum [$\nu_{max.}$ 1695 and 1686 (C=O) and

---

* Baddeley and Wrench (ref. 10) carried out a similar experiment but neither measured the carbon monoxide nor detected the *trans*-decalin.

[37] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugash, *J. Amer. Chem. Soc.*, 1960, **82**, 4719.

[38] H. Stetter and E. Rauscher, *Chem. Ber.*, 1960, **93**, 1161. No details given.

[39] Amer. Petroleum Inst. Research Project 44. Infrared Spectral Data no. 2146.

[40] Ref. 38, no. 1087.

[41] S. M. McElvain and D. C. Remy, *J. Amer. Chem. Soc.*, 1960, **82**, 3960.

[42] A. Zlatkis and E. A. Smith, *Canad. J. Chem.*, 1951, **29**, 162.

[43] H. Christol and G. Solladie, *Bull. Soc. chim. France*, 1966, 1299, 1307.

[44] W. B. Moniz and J. A. Dixon, *J. Amer. Chem. Soc.*, 1961, **83**, 1671.

1022 (cyclopropane ring) cm.$^{-1}$ (lit.,[45] 1680 and 1022 cm.$^{-1}$) indicated the presence of two phenyl ketones (3 : 2). One of these may have been 1-benzoyl-1-methylcyclopropane (lit.,[45] prepared from 4-chloro-2-methylbutyrophenone, b.p. 93—97°/2·5 mm.); the ^{1}H n.m.r. spectrum included a symmetrical set of signals with centre at τ 9·10, typical of a 1,1-disubstituted cyclopropane (AA′BB′ structure, $CH_2\cdot CH_2$),[46] with the reduced intensity to be expected from a mixture; other signals at 8·65 (s, Me), 2·3 and 2·6 (5H, multiples typical of a phenyl ketone, intensity consistent with both components of the mixture containing the group), and some low intensity unidentified signals overlapping those at 9·10.

(ii) *In anisole.* The product was 1-p-*methoxybenzoyl*-1-*methylcyclopropane* (64%), b.p. 149—150°/10 mm. (Found: C, 75·7; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), *oxime*, m.p. 127—128° (needles from dilute methanol) (Found: C, 70·4; H, 7·4; N, 6·8. $C_{12}H_{15}NO_2$ requires C, 70·2; H, 7·3; N, 6·9%). The ^{1}H n.m.r. spectrum of the ketone showed signals at τ 8·60 (s, Me), 6·60 (s, OMe), 2·23 and 3·19 (AB structure, 4 aromatic H, *J* 8·5 c./sec.), and some symmetrical absorptions with centre at 9·12 (AA′BB′, $CH_2\cdot CH_2$) resembling those of the corresponding protons of 1-phenylcyclopropanecarboxylic acid.[47]

(g) *With* 1-*methylcyclobutanecarbonyl chloride.* (i) *In benzene.* This acid chloride (4·74 g.) yielded carbon monoxide (51%) and, after work-up, the following fractions: (i) b.p. 90—130°/14 mm. (0·2 g.), consisting of several components one of which was benzaldehyde; (ii) b.p. 130—140°/14 mm. (0·63 g.) shown by g.l.c. (polyethylene glycol at 180°) to contain four carbonyl derivatives; the ^{1}H n.m.r. spectrum of the mixture showed no signals corresponding to those of 1-benzoyl-1-methylcyclobutane described above; (iii) b.p. 90—130°/0·2 mm. (0·8 g.); and (iv) b.p. 130—140°/0·2 mm. (1·0 g.). The i.r. spectra of fractions (iii) and (iv) exhibited multiple peaks in the carbonyl region and were probably mixtures. No fraction corresponding to 1-methyl-1-phenylcyclobutane was observed.

(ii) *In anisole.* Carbon monoxide was not evolved. The principal product was 1-p-*methoxybenzoyl*-1-*methylcyclobutane* (70%), b.p. 109—110°/0·04 mm., 106—107°/0·03 mm. (Found: C, 76·6; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·9%); *oxime*, m.p. 142—142·5° (needles from aqueous ethanol) (Found: C, 71·5; H, 7·9; N, 6·5. $C_{13}H_{17}NO_2$ requires C, 71·2; H, 7·8; N, 6·4%). The ^{1}H n.m.r. spectrum of the ketone showed peaks at τ 8·75 (s, Me), 6·30 (s, OMe), 2·0br ($CH_2\cdot CH_2\cdot CH_2$), and 2·85 and 3·28 (AB structure, 4 aromatic H, *J* 9·0 c./sec.).

(h) *With* 1-*Methylcyclopentanecarbonyl chloride.* See ref. 15.

(i) *With* 2-*methylnorbornane*-2-exo-*carbonyl chloride.* (i) *In benzene.* A solution of the acid chloride (5·92 g., 0·0343 mole) in benzene (5 c.c.) was added to a suspension of aluminium chloride (5·05 g., 0·038 mole) in benzene (30 c.c.) with continuous stirring. After the vigorous evolution of carbon monoxide, the mixture separated into two layers and was decomposed in the usual way. Two fractions were obtained: (i) b.p. 125—130°/13 mm. (1·71 g.) (Found: C, 88·9; H, 8·8%) which (g.l.c. on didecyl phthalate at 170°) consisted mainly of two substances (4 : 1), together with a trace of benzaldehyde; (ii) b.p. 105—125°/0·15 mm. (0·75 g.) which deposited a *hydrocarbon*, m.p. 132—134° (from methanol) (Found: C, 91·2; H, 8·4%. M, 240). Apart from absorptions at τ 8·70 (s, Me) and at 3·03 (s, Ph_2), the ^{1}H n.m.r. spectrum was not very informative. There were unresolved groups of signals at *ca.* 6·8 (1H) and 7·8—9·9. The latter overlapped with the methyl signal and presumably included absorptions due to bridgehead protons.[48] The presence of two phenyl groups per molecule suggested the molecular formula $C_{20}H_{22}$ (requires C, 91·6; H, 8·4%. *M*, 262).

(ii) *In anisole.* Carbon monoxide was not eliminated and the sole product isolated was 2-exo-p-*methoxybenzoyl*-2-*methylnorbornane* (84%), b.p. 150—151°/0·15 mm., 142—144°/0·07 mm. (Found: C, 78·7; H, 8·4. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·3%). The structure was as assigned because ketone-forming Friedel-Crafts reactions on tertiary acid chlorides do not alter the configurations of the carbon atoms to which the chlorocarbonyl groups are attached.[13] The ^{1}H n.m.r. spectrum also largely confirmed the structure: τ 8·68 (s, Me), 6·22 (s, OMe), 3·19 and 2·17 (AB structure, 4 aromatic H, *J* 9 c./sec.), some unresolved signals at 7·2—7·9 partly due to the bridgehead protons,[48] and other unresolved signals 0·8—0·9. There were no signals at 5·17 characteristic of the 2-*exo*-hydrogen.[48]

(j) *With* 2-*methylnorbornane*-2-endo-*carbonyl chloride.* (i) *In benzene.* The mixture of acid chloride (5·47 g., 0·0317 mole) and catalyst (4·8 g., 0·036 mole) in benzene (28 c.c.) afforded carbon monoxide (80%) and two fractions identical (i.r. spectra and g.l.c.) with those obtained from the *exo*-derivative: (i) b.p. 125—130°/10 mm. (1·55 g.) (Found: C, 89·2; H, 8·8%) and (ii) b.p. 100—130°/0·05 mm. (1·04 g.); the crystalline component separated from methanol as needles, m.p. 134—135° (Found: C, 91·0; H, 8·4%).

TABLE 3

I.r. absorptions (2000—667 cm.$^{-1}$) of phenyl (m.p. 132—135°) and of *p*-methoxybenzoyl derivatives of bornane (*a*) -2-*exo*- and (*b*) -2-*endo*-carbonyl chlorides

Phenyl [(*a*) ≡ (*b*)] (KCl disc)		*p*-Methoxybenzoyl (film)			
		(*a*)	(*b*)	(*a*)	(*b*)
1595ms	990sh	1667s	1667s	1110sh	1114w
1490s	982w	1605s	1605s	1029m	1033m
1443s	968sh	1575sh	1575sh	*970*m	*980*m
1387w	930w	1513m	1513m	*944*w	*961*w
1366w	926w	*1453*m	*1452*m	*926*w	*948*w
1331ms	909w	1418w	1418w		932w
1314w	899w	1374w	1379w	909w	906w
1261w	847w	1309m	1312m	885w	876w
1235w	834w	1253s	1258s	843w	851m
1209w	801w	1238sh	1238m	839w	840w
1183w	787w	1227sh	1227sh	*812*w	*801*m
1149w	782ms	*1170*m	*1183*w,sh	768w	769m
1096w	760s	1161s	1161s	695w	699w
1066ms	729s	1129w	1129w		
1054sh	694s				
1031ms					

Italicised figures indicate corresponding frequencies in (*a*) and (*b*).

(ii) *In anisole.* The reaction yielded 2-endo-p-*methoxybenzoyl*-2-*methylnorbornane* (81%), b.p. 140°/0·04 mm. (Found: C, 79·0; H, 8·3. $C_{16}H_{20}O_2$ requires C, 78·7; H, 8·3%), different from the corresponding *exo*-compound.

---

[45] G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Amer. Chem. Soc.*, 1959, **81**, 1660.

[46] Compare A. A. Pavia, J. Wylde, R. Wylde, and E. Arnal, *Bull. Soc. chim. France*, 1965, 2709.

[47] H. M. Hutton and T. Schaefer, *Canad. J. Chem.*, 1963, **41**, 2429.

[48] E. W. C. Wong and C. C. Lee, *Canad. J. Chem.*, 1964, **42**, 1245.

The respective i.r. spectra were not identical (see Table 3). A comparison was also carried out by balancing the absorptions at 2000 cm.$^{-1}$ when the two compounds were placed in the reference and sample beams respectively. Marked difference in intensity were noted at 1253, 1172, 1157, 1126, 964, and 924 cm.$^{-1}$. The ^{1}H n.m.r. spectrum of the *endo*-compound showed displaced absorptions at τ 8·63 (s, Me), 6·23 (s, OMe), and 3·23 and 2·22 (AB structure, 4 aromatic H, J 8·0 c./sec.), and similar displacements in the unresolved absorptions.

(k) *With norbornane*-2-endo-*carbonyl chloride*. There was no reaction in chloroform solution. In benzene the reaction afforded 2-endo-*benzoylnorbornane* (85%), b.p. 160°/11 mm., m.p. *ca.* 20° (Found: C, 84·2; H, 8·2. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%), which g.l.c. (silicone grease at 250°) showed to be the only product. Carbon monoxide was not liberated.

We thank the S.R.C. for a grant (to D. G. P.).

[8/381 *Received, March* 18*th*, 1968]