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REACTION OF DILITHIUM BENZOPHENONE, DILITHIUM 9-FLUORENONE AND THE LITHIUM SALT OF BENZOPHENONE KETYL WITH CHLORIDES AND ANHYDRIDES OF CARBOXYLIC ACIDS

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Summary

The reaction of dilithium benzophenone and the lithium salt of benzophenone ketyl with anhydrides and chlorides of benzoic and acetic acid and the reaction of dilithium 9-fluorenone with acetic anhydride were investigated. In addition to the expected products $Ar_2C(COR)OCOR$, products of the type $Ar_2C{=}CR(OCOR)$ were also obtained, and in the case of reactions with acetyl chloride and acetic anhydride, products of the type $Ar_2CH(OCOR)$. ESR studies showed that ketyl is formed in the reaction of dilithium benzophenone with acetic anhydride, and the CIDNP method revealed that benzhydryl acetate is formed, at least in part, by hydrogen transfer to a free radical produced by O-acetylation of the ketyl. The results suggest a competition between addition and electron transfer reactions.

Introduction

The compounds formed by the reaction of 1 mole of benzophenone or other diaryl ketones with two g-atoms of alkali metal react with electrophilic substrates mostly as monofunctional organometallic agents [1—5]. In the reactions with alkylating agents, a competition between C- and O-alkylation and the alkylation of the aromatic nucleus was observed [1,4,5]. Only the product of the C-addition was isolated from the reactions with other reagents such as aldehydes, ketones, dialkyl carbonates, carbon dioxide and nitriles [2,3]. However, the low yields and their strong dependence on the reaction conditions suggest that the reaction is complex and that competing reaction paths exist.

Results and discussion

Products of the reactions of dilithium benzophenone and the lithium salt of benzophenone ketyl with acylating agents

It was of interest to investigate the reactions with anhydrides and chlorides of carboxylic acids, because these are more electrophilic than the substrates previously studied. The reaction may then be considered the limiting case of the reaction of the dimetallo compound of the diaryl ketone with an electrophile. In addition, since the products are acyl derivatives, they are expected to be stable and one need not consider complicating reactions during the final hydrolysis of the reaction mixture.

The dilithium benzophenone reaction was compared with the analogous ketyl reaction. In the product mixtures formed from these compounds with acetic anhydride, in addition to the recovered benzophenone, the following were identified: 1,1-diphenyl-2-oxopropyl acetate (Ia), 2,2-diphenyl-1-methylethenyl acetate (IIa), and benzhydryl acetate (III). The mixtures also contained small amounts of other products, which could not be isolated by preparative chromatography, but were shown not to interfere with the main products in the analytical liquid—liquid chromatography.

Table 1 lists the yields of products in the reaction of dilithium benzophenone and the lithium salt of benzophenone ketyl with acetic anhydride and acetyl chloride.

Benzoic anhydride or benzoyl chloride reacted with the lithium salt of benzophenone ketyl and with dilithium benzophenone in the same way as acetic anhydride, yielding 1,1,2-triphenyl-2-oxoethyl benzoate (Ib) and 1,2,2-triphenylethenyl benzoate (IIb). However, the product mixtures are more com-

TABLE 1

ANALYTICAL CHROMATOGRAPHY OF PRODUCTS FROM THE REACTIONS OF LITHIUM SALT OF BENZOPHENONE KETYL AND DILITHIUM BENZOPHENONE WITH ACETIC ANHYDRIDE AND ACETYL CHLORIDE (VALUES BP, Ia, IIa AND III ARE IN % OF THE ORIGINAL BENZOPHENONE) [a]

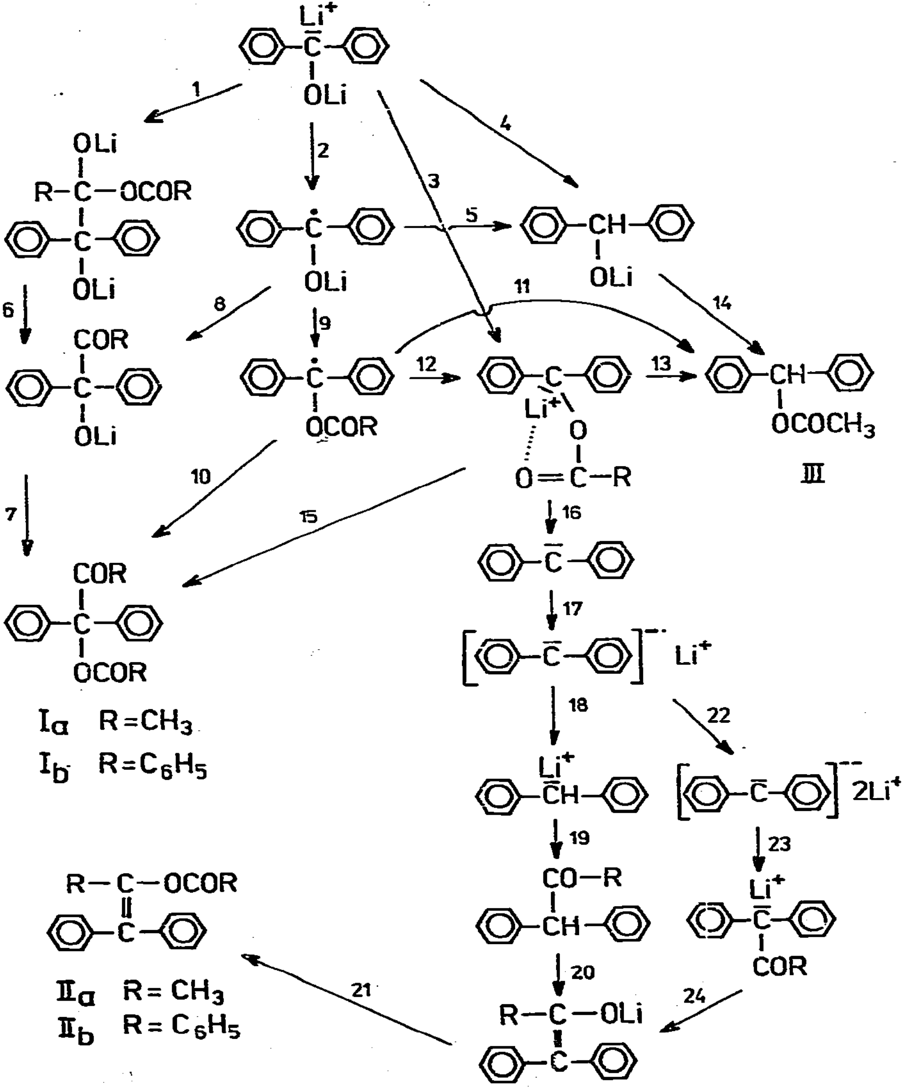
Reagent (mmol)	Substrate (mmol)	BP	Ia	IIa	III
Ac_2O (31.8)	$BP^{-}\cdot Li^{+}$ [b] (14.4)	52.7	33.2	0.2	7.0
AcCl (33.4)	$BP^{-}\cdot Li^{+}$ [b] (15.2)	38.1	32.0	0.1	1.7
Ac_2O (31.8)	$BP^{2-}2Li^{+}$ [b] (15.1)	9.8	36.0	5.7	24.5
Ac_2O [c] (13.8)	$BP^{2-}2Li^{+}$ (15.9)	7.0	21.9	6.0	49.5
AcCl (33.4)	$BP^{2-}2Li^{+}$ [b] (15.1)	9.5	29.1	3.0	19.5

[a] The lithium compound of benzophenone was always prepared in 55 ml of THF. the acetylating agent was diluted with 20 ml of THF before added to the reaction. The reaction was performed in the same way as in the preparative experiments. [b] The solution of ketyl or dimetallo compound added to the acetylating agent. [c] The solution of acetanhydride added to the dimetallo compound. BP - benzophenone, Ac_2O - acetic anhydride, AcCl - acetyl chloride.

plex in this case, and this causes difficulties in the preparative chromatography, and so these reactions were not studied in detail.

Investigation of the reaction of dilithium benzophenone and the lithium salt of benzophenone ketyl with acetic anhydride by ESR and CIDNP

Scheme 1 summarizes possible mechanisms of the reaction between dilithium benzophenone and the lithium salt of benzophenone ketyl. Two competitions have to be considered in the case of the dilithium benzophenone.



SCHEME 1

1) Competition between direct addition (1, 3) and electron transfer (2).

2) In the addition reaction, competition between attack at carbon atom (1) and attack at oxygen (3).

ESR studies showed that at least part of the products from the reaction of dilithium benzophenone is formed by an electron-transfer mechanism. During the mixing of a THF solution of dilithium benzophenone with a solution of acetic anhydride, we observed the ESR spectrum of benzophenone ketyl, with an intensity 72 times as high as that of the spectrum of the residual ketyl, in the dilithium benzophenone solution. This proved that the ketyl is a reaction intermediate.

Consequently, the formation of compound Ia from the dilithium benzophenone must involve a competition between, on the one hand the quasi-ionic processes 1—6—7 and 3—15, and on the other hand processes 2—8—7 or 2—9—10, where the initial step is a one-electron transfer. Processes 8 and 10 then represent combination reactions of the radical $CH_3CO^{\bullet}$, which is generated by the decomposition of an anion-radical formed by one-electron transfer from the dilithium benzophenone to acetic anhydride (2).

The mechanism for the formation of Ia from ketyl may involve the above-mentioned reaction of ketyl with acetic anhydride [6], in which the ketyl was generated by electroreduction of benzophenone in an acetonitrile medium. This reaction also led to Ia, which was obtained in a yield of 66%, while by-products were not isolated. A polarographic study of benzophenone in this medium revealed that addition of acetic anhydride results in a moderate decrease of the half-wave potential of the first wave and in increase in the current (a fivefold excess of acetic anhydride causing a doubling of the current). The second wave, corresponding to the reduction to the dianion, which is of low intensity because of the reaction of this species with acetonitrile, was entirely suppressed under these conditions. From this, the authors assumed initial one-electron reduction of benzophenone and acylation of the originated ketyl, followed by reduction of the acylated species to a C-anion, and its final acylation to compound Ia, i.e. the reaction path indicated in our scheme by processes 9—12—15.

Some of the proposed pathways for the formation of compound III may be confirmed by CIDNP. On mixing a THF solution of the lithium salt of the benzophenone ketyl with acetic anhydride, a weak emission corresponding to the CH proton of benzhydryl acetate was observed in addition to a strong emission from the aromatic protons. Unfortunately, the spectra were poor due to partial precipitation of lithium acetate during the reaction. Well resolved spectra were obtained when we used solutions of the sodium salt of ketyl and the disodium benzophenone in 1,2-dimethoxyethane with addition of 18-Crown-6 to the acetic anhydride solution. In that case, a significant signal from the benzhydryl hydrogen was observed both in the reaction of ketyl and of the dimetallo compound (Fig. 1). This signal corresponds to the reaction pathway 2—9—11. The pathway 2—5—14 should lead to an emission from the hydrogen of benzhydryl alkoxide, which would be expected at a rather different field. On the other hand, the pathway 4—14 corresponds to the reaction of the C-anion with a protic acid which should lead to no CIDNP. A similar argument holds for step 13 in the alternative reaction pathways 2—9—12—13 or 3—13.

The significantly higher yield of compound III in the reaction of the dimetallo compound as compared with the ketyl reaction led us to assume that 2—9—11 is not the only pathway for the formation of compound III. A similar

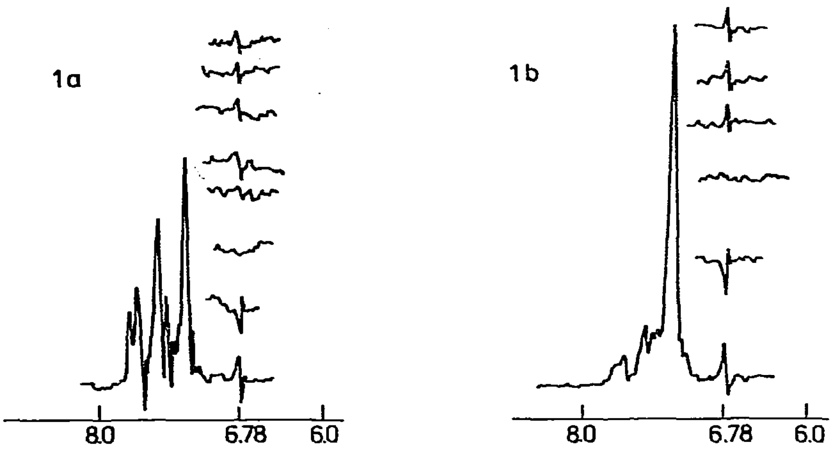


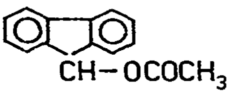
Fig. 1. CIDNP effect of the reaction of sodium salt of benzophenone ketyl (1a) and disodium benzophenone (1b) with acetic anhydride.

increase in yield of the reaction of the dimetallo compound compared with that of ketyl was observed with compound IIa, which is formed in the reaction of ketyl only in very small amount. The formation of this compound may be related to the competition between the C- and O-acylation of the dimetallic compound. By analogy to the behaviour of geminal lithio methyl halides [7—9], the O-acylation product should be highly unstable, undergo α-elimination, and generate a carbene.

α-Elimination to form a carbene has been recently assumed [10] to accompany the rearrangement of metallated benzyl or benzhydryl ethers to substituted benzyl or benzhydryl alkoxides [11,12], e.g., the formation of diphenylmethane and phenol in the metallation of benzhydryl phenyl ether. In the case of the metallated benzhydryl ester, the α-elimination is further facilitated by the formation of a five-membered cyclic transition state with lithium coordinated to the carbonyl oxygen.

It is possible that the α-elimination does not proceed in the given case via a free carbene but only via a carbenoid transition state [9]. As expected, the electron deficient carbene or carbenoid may be readily metallated by the dianion in the reaction mixture to an anion-radical (17) and can yield compound IIa either by pathway 18—21 or by pathway 22—23—24—21. The presence of the anion-radical of diphenylcarbene has been recently proved in a study of the cyclic voltammetry of diphenyldiazomethane [13]. Formation of the dianion of (2,2′-biphenyldiyl)-carbene has also been assumed in the reaction of dibromofluorene with naphthalene sodium [14]. Reactions analogous to steps 19—21 have been previously reported [15].

The O-acyl anion formed by reaction 3 might also lead to compound III by process 13, in addition to the above mentioned carbenoid reaction. This would explain the increased yield of both these products in the reaction of dilithium benzophenone as compared to the reaction of the lithium salt of the benzophenone ketyl. Another explanation of the enhanced yield of compound III may be pathway 4—14 which is supported by the strongly nucleophilic character of the dilithium benzophenone.



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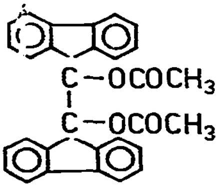
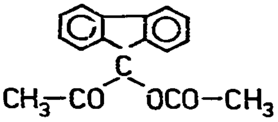
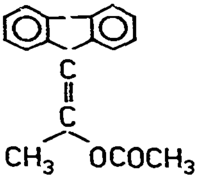


V



VI



VII

Fig. 2. Structure of compounds IV—VII.

Products of the reaction of dilithium 9-fluorenone with acetic anhydride

Dilithium 9-fluorenone reacts with acetic anhydride in a similar way to dilithium benzophenone. 9-Fluorenyl acetate (IV), 9,9′-difluoren-9,9′-diyldiacetate (V), 9-acetyl-9-fluorenyl acetate (VI) and 1-(9-fluorenylidene) ethyl acetate (VII) and a small amount of recovered 9-fluorenone were isolated from the reaction mixture (Fig. 2). In addition to these products, fluorene was formed in a yield of 0.18% (based on the initial 9-fluorenone), while the hydrolysate of the dilithium 9-fluorenone solution employed contained at most 0.03% of fluorene. This confirms the formation of fluorene in the reaction of dilithium 9-fluorenone with acetic anhydride. Fluorene may be expected as a by-product in the carbene-generating α-elimination assumed to explain the formation of VII.

Conclusions

(1) Initial O-acylation was demonstrated by identification of the products of Type II, the formation of which cannot be accounted for in terms of a primary C-acylation.

(2) The competition between an electron transfer and a quasiionic addition reaction was demonstrated, especially by the formation of ketyl in the reaction by ESR and by the CIDNP effect in the partial reaction.

Experimental

Chemicals

The final purification of THF by $LiAlH_4$ and of 1,2-dimethoxyethane by Na, the preparation of metallo compounds of benzophenone and their handling were carried out under argon. The solutions of dilithium benzophenone were prepared by reduction of THF solutions of benzophenone with an excess of lithium ($Li/C_{13}H_{10}O = 4$) at room temperature for 3 h with stirring. The used lithium metal was hammered under Nujol and rinsed with THF under argon.

Methods

If not stated otherwise, the samples for analysis were dried at 80°C and 60 Pa for 4 h. Silica gel 60—120 μm containing 12% water was used in the preparative chromatography. Except for the separation of reaction mixtures from the reaction of the lithium salt of benzophenone ketyl with acetic anhydride and the reaction of dilithium fluorenone with acetic anhydride, the chromatography was carried out with an eluent of higher polarity than required for the stepwise elution of individual fractions. Only sharp fractions were worked up, and their purities confirmed by TLC or by analytical liquid chromatography.

The analytical liquid chromatography was carried out using a glass column [16] 30 cm long and an ID of 3 mm packed with 18 μm silica gel beads [17] with a specific surface area of 300 m^2/g. The UV detector (Development Workshops, Czechoslovak Academy of Sciences) operating at a wavelength of 254 nm was used for detection. The column was packed by a standard balance slurry technique and impregnated by washing with the saturated solution of polyoxyethylene 400 in a 1 : 1 mixture of ether and heptane. The elution in the chromatographic analysis (Table 1) was carried out with heptane saturated with polyoxyethylene 400 at a flow 6.5 ml/h. The same equipment and system were used in the determination of fluorene in the reaction mixture and in the hydrolysate of dilithium 9-fluorenone.

The ^1H NMR spectra were measured with a PS 100 (Jeol) spectrometer at 100 MHz, the ESR spectra with a JES-PE-3X (Jeol) instrument, and the IR spectra with a UR 10 spectrometer in KBr pellets, unless otherwise stated.

The reaction of the lithium salt of benzophenone ketyl with acetic anhydride

A solution (55 ml) containing 14 mmol of lithium salt of benzophenone ketyl in 55 ml THF was added during 30 min with stirring to a solution of 1.5 ml (15.9 mmol) of acetic anhydride in 10 ml THF, and the mixture was stirred for further 30 min. The THF was evaporated in vacuum and the residue was dispersed in 30 ml water and extracted three times with 50 ml of ether. The combined ether extracts were dried over magnesium sulphate, evaporated in vacuum (yield 2.96 g), and chromatographed on silica gel with benzene as eluent. TLC showed that the first fraction contained benzophenone mixed with a very small amount of a non isolated compound; the subsequent fraction (0.99 g after evaporation) contained a mixture of benzophenone and benzhydryl acetate. The IR spectrum of this mixture (measured in CCl_4) contained all the bands of both these compounds and no additional bands. The mass spectrum also exhibited only the molecular ions of these compounds and their fragments. The same composition of the fraction was confirmed also by analytical liquid chromatography. The residue after evaporation of the third fraction (1.21 g, compound Ia) was distilled in vacuum 60 Pa. Found: C, 76.09; H, 6.07, $C_{17}H_{16}O_3$ (268.3) calcd.: C, 76.11; H, 6.01%. IR spectrum: 3000—3100 (aromatic CH), 2800—3000 (CH_3), 1760 (OCO), 1740 (CO), 1500—1700 (skeletal aromatics), 710, 770 cm^{-1} (CH, out-of-plane vibrations of arom. nuclei); ^1H-NMR spectrum, δ: 2.00, 2.10 (CH_3, 2 × 3 H); 7.2—7.5 ppm (aromatics, 10 H). Mass spectrum: for $C_{17}H_{16}O_3$ calculated 268.1099, found 268.1092; fragments (*m/e*): 225, 183, 165, 105. The IR spectrum has been reported [6]; the frequencies of some bands did not agree with the published values, possibly because of different measuring techniques.

The reaction of dilithium benzophenone with acetic anhydride

A solution of 6 ml (63.6 mmol) of acetic anhydride in 40 ml THF was added with stirring to a solution of 31.7 mmol dilithium benzophenone in 115 ml THF. After 30 min stirring, the mixture was worked up as in the preceding case. The yield of evaporated ether extracts was 6.8 g. The chromatography of 5.45 g of products on a 300-fold excess of silica gel with benzene as eluent (after elution with 13 l benzene, 1% of ether added; after 29 l, 1.5% of ether added) gave 0.163 g of 2,2-diphenyl-1-methylethenyl acetate IIa after evaporation of the first fraction. Found: C, 80.55; H, 6.34, $C_{17}H_{16}O_2$ (252.3) calcd.: C, 80.92; H, 6.36%. Mass spectrum: for $C_{17}H_{16}O_2$ calculated 252.1150, found 252.1140; fragments (*m/e*) 210, 182, 167, 165. IR: 3000—3100 (aromatic CH), 2800—3000 (CH_3), 1750 (OCO), 1500—1700 (skeletal aromatics, C=C), 710, 770 cm^{-1} (CH, out-of-plane vibrations of aromatic nuclei). ^1H NMR δ: 1.85, 1.99 (CH_3, 2 × 3 H), 7.13, 7.19 ppm (aromatics, 10 H). Further fractions contained a mixture of benzophenone and benzhydryl acetate which were not separated under our conditions. Compound Ia (0.4 g) was isolated from the last fraction, and gave the same IR spectrum and chromatographic behaviour as the product obtained from the reaction of benzophenone ketyl with acetic anhydride.

The reaction of lithium salt of benzophenone ketyl with benzoic anhydride

A solution of 15.7 mmol lithium salt of benzophenone ketyl in 57 ml THF was added to a solution of 7.189 g (31.8 mmol) benzoic anhydride in 20 ml THF. After 30 min of stirring, the mixture was worked up as above. The yield of evaporated ether extracts was 7.69 g. Part of the product (5—6 g) was chromatographed on silica gel using a 95 : 5 mixture of petroleum ether and ether. The residues after evaporation of the 1st and 2nd fraction were refined by further chromatography on a 300-fold quantity of silica gel with benzene as the eluent. Crystallization of the main fraction (chromatography of the residue of 1st fraction) gave a small amount (44 mg) of a compound of m.p. 152°C which had the same IR spectrum and chromatographic behaviour as the known 1,2,2-triphenylethenyl benzoate (IIb) [18]. The main portions from the repeated chromatography of 2nd fraction was treated analogously to yield 0.2 g of the compound Ib; m.p. 145—6°C. Found: C, 82.61; H, 5.70, $C_{27}H_{20}O_3$ (392.4) calcd.: C, 82.63; H, 5.14%. The IR spectrum exhibited bands at 1730 (OCO) and 1700 cm^{-1} (CO). The mass spectrum reveals a small peak at *m/e* 392 and an intense fragment $C_{20}H_{15}O_2$ corresponding with loss of benzoyl; calculated: 287.1072, found: 287.1074.

The reaction of dilithium benzophenone with benzoyl chloride

A solution of 29.2 mmol dilithium benzophenone in 115 ml THF was added to a solution of 8.913 g (63.4 mmol) benzoyl chloride in 40 ml THF. After 30 min stirring, the mixture was worked up as in the preceding cases. The yield of evaporated ether extracts was 12.02 g. A part of the residue (10.58 g) was chromatographed on the 200-fold excess of silica gel with benzene as an eluent. The residue after evaporation of the first fraction was recrystallized from ethanol to give 0.28 g of a compound melting at 153—4°C, which is identical, (mixed m.p. and IR spectrum) with the known compound IIb [18]. The residue after evaporation of a further fraction (3.07 g) was shown by TLC to contain the compound Ib slightly contaminated by another compound.

The reaction of dilithium 9-fluorenone with acetic anhydride

A solution of 6 ml (63.6 mmol) acetic anhydride in 40 ml THF was added to a solution of 30.4 mmol dilithium 9-fluorenone in 110 ml THF. After 30 min stirring the mixture was worked up as above. The yield of evaporated ether extracts was 7.6 g. Part of the product (6.8 g) was chromatographed on a 300-fold amount of silica gel initially with petroleum ether as an eluent, the petroleum ether then being gradually mixed with ether: 0% up to 2 l, 1% up to 27 l, 1.2% up to 29 l, 3% up to 63.5 l, 5% up to 71.5 l, 10% up to 83 l, and then 20%. Fluorene was identified in the evaporated first fraction by means of mass spectrometry. The evaporated second fraction (0.9839 g) contained a mixture of 9-fluorenone and 9-fluorenyl acetate (IV). Crystallization from ethanol yielded 0.676 g, (11%) of fluorenyl acetate of m.p. 70—71.5°C; (lit. [19] 70°). Found: C, 80.08; H, 5.34; $C_{15}H_{12}O_2$ (224.2) calcd.: C, 80.33; H, 5.40%. Mass spectrum: for $C_{15}H_{12}O_2$ calcd. 224.0837, found 224.0844. ^{1}H NMR, δ: 2.16 (CH_3, 3 H), 6.78 (CH, 1 H), multiplets 7.1, 7.7 ppm (aromatics, 8 H). The compound VII was obtained by two crystallizations of the third fraction (0.534 g, 8%) from ethanol; m.p. 97.5—98.5°C (lit. [15] 97—98°C). Found: C, 82.23; H, 5.64; $C_{17}H_{14}O_2$ (250.3) calcd.: C, 81.58; H, 5.64%. Mass spectrum exhibited *m/e* 250.0981; $C_{17}H_{14}O_2$ calculated: 250.0994. IR spectrum: 1750 (OCO), 1500—1700 cm^{-1} (skeletal aromatics, C=C), 760 cm^{-1} (out-of-plane vibrations of 1,2-disubstituted aromatic nucleus). ^{1}H NMR, δ: 2.37, 2.60 (CH_3, 2 × 3 H), multiplets 7.3, 7.7 ppm (aromatics, 8 H). The compound VI was obtained by crystallization of the evaporated fourth fraction (1.349 g, 18%) from ethanol; m.p. 98.5—100°C. Found: C, 76.73; H, 5.30; $C_{17}H_{14}O_3$ (266.3) calcd.: C, 76.67; H, 5.30%. Mass spectrum: for $C_{17}H_{14}O_3$ calculated 266.0943, found 266.0940; fragments (*m/e*) 223, 181. IR spectrum: 3000—3100 (CH, stretching aromatics), 2800—3000 (CH_3), 1750 (OCO), 1730 cm^{-1} (CO). ^{1}H NMR δ: 1.82, 2.15 (CH_3, 2 × 3 H), multiplets: 7.2, 7.7 ppm (aromatics, 8H).

Two further fractions contained compounds which decomposed during isolation. Compound V was obtained by crystallization from ethanol of the residue obtained by evaporation of the last fraction (0.327 g, 5%); it sublimed during attempts to determine the melting point. Found: C, 81.00; H, 5.00; $C_{30}H_{22}O_4$ (446.5) calcd.: C, 80.70; H, 4.97%. The mass spectrum exhibited *m/e* 446.1510, calculated for $C_{30}H_{22}O_4$ 446.1518; fragments (*m/e*) 223, 181. IR spectrum: 3000—3100 cm^{-1} (CH_3), 1750 cm^{-1} (OCO). ^{1}H NMR spectrum, δ: 2.13 ppm (CH_3, 3H), multiplet 6.5—7.4 ppm (aromatics, 8H).

Measurement of ESR signal during the reaction of dilithium benzophenone with acetic anhydride

A solution of dilithium benzophenone was prepared by the reaction of 0.227 g benzophenone in 25 ml THF with the excess of lithium for 3 h. The solution of acetic anhydride contained 0.1 ml in 25 ml THF. First, the spin content in 0.5 ml of the solution of dilithium benzophenone was determined. Then, 0.5 ml of acetic anhydride solution was added, the liquid was agitated for 2 s by bubbling nitrogen through it and the spin content was measured again. After addition of acetic anhydride, the spin content in the sample after recalculation to the same concentration of dilithium benzophenone was 72-times higher. The splitting constants agreed within experimental error with the value published for the lithium salt of benzophenone ketyl [20].

CIDNP study of the reaction of disodium benzophenone and the sodium salt of benzophenone ketyl with acetic anhydride

Solutions employed: The solution of disodium benzophenone was prepared by reduction of part (12.5 ml) of the solution containing 0.515 g benzophenone in 25 ml 1,2-dimethoxyethane with an excess of sodium (0.4 g for 3 h at 20° C). The solution of the sodium salt of benzophenone ketyl was prepared by mixing equal parts of the above solution and the original benzophenone solution. The solution of the acetylating reagent was prepared by dissolution of 0.08 ml acetic anhydride and 0.2 g 18-Crown-6 in 1.8 ml 1,2-dimethoxyethane.

The measuring technique was analogous to the procedure [21] used in investigation of the reaction of naphthalene sodium with water. The solution of the sodium salt of benzophenone ketyl (0.25 ml; experiment 1a) or the same amount of the solution of disodium benzophenone (experiment 1b) was delivered from a syringe into the NMR cell which was closed by a septum and flushed with argon. The cell was then placed in an Helmholtz coil of magnetic field intensity 60 G, 0.25 ml of the solution of the acetylating reagent was added, the cell was inverted to mix the contents, and then placed in the spectrometer; measurements were started not more than 8 s after addition of the acetylating reagent. The position of the measured band of benzhydryl hydrogen was confirmed by addition of 4 µl of compound III to the equilibrium mixture following complete reaction.

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