[Contribution from the Sterling Chemistry Laboratory, Yale University]

REACTION OF N,N-DIALKYLBENZAMIDES WITH SODIUM

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During an investigation of some aspects of the mixed acyloin reaction it was found that aliphatic N,N-dialkylamides were unaffected by the action of sodium in a refluxing benzene solution (1). The aromatic analogs, the N,N-dialkylbenzamides, however, readily reacted under the same conditions to yield a variety of interesting products.

The sodation of N,N-dimethylbenzamide (Ia) in anhydrous benzene yielded the following products: benzoin (II) in 5.5% yield; phenylphthalide (III) in 2% yield; *p,p'*-bis(N,N-dimethylcarboxamido)benzopinacol (IVa) in 3.5% yield, the proof of structure of which is given below; benzaldehyde (V) in trace amount, identified by its 2,4-dinitrophenylhydrazone; and benzoic acid (VI) in 5% yield. Oxidation of the neutral residue remaining after isolation of the above products yielded 4-carboxybenzophenone in a yield of 12% based on the weight of Ia used.

A similar sodation of N,N-diethylbenzamide (Ib) gave the following products in several runs: phenylphthalide (III) in 5% yield: *p,p'*-bis(N,N-diethylcarboxamido)benzopinacol (IVb) in 1–2% yield; benzoic acid (VI) in 2–6% yield; and anthraquinone (VII) in 2–10% yield.

The substituted benzopinacol structure was assigned to IVa and IVb on the basis of their analysis, low solubility, high melting point, and infrared spectra. These latter data, shown in Figure 1, clearly indicate the presence of carboxamido groups, *para* substitution, and hydroxyl groups. The hydroxyl groups were shown to be tertiary since the substance could not be readily acetylated or oxidized by Oppenauer's method (2). Synthesis of IVa and IVb was first attempted by the sodium reduction of the 4-N,N-dialkylcarboxamidobenzophenones (3), VIIIa and VIIIb, which were prepared from 4-carboxybenzophenone by reaction of the acid chloride with the dialkylamine. Though a deep blue color characteristic of the expected metal ketyl intermediate (3) was observed during the reaction, no *p,p'*-bis(N,N-dialkylcarboxamido)benzopinacol (IV) could be isolated; instead, a mixture, separable only with difficulty (3), of VIII and 4-N,N-dialkylcarboxamidobenzohydrol was obtained. Presumably these products arose from the cleavage of the sodium pinacolate during the reaction.

An attempted bimolecular reduction of VIII by magnesium subiodide (5) was also unsuccessful, the starting material being recovered unchanged. It is apparent that not only is magnesium subiodide a less reactive radical than metallic sodium, but that the ketonic carbonyl group of VIII is less reactive

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than that of benzophenones which possess electron-releasing substituents (5). It was found also that ethyl propionate was unreactive toward magnesium subiodide, while it is reported that ethyl benzoate yields benzoin under the same conditions (6). This further illustrates the difference in reactivity of aliphatic and aromatic carbonyl groups toward active metals.

Syntheses of IVa and IVb were finally achieved by the irradiation of propanol-2 solutions of VIIIa and VIIIb with ultraviolet light (7). However, the products of the irradiations, though similar in analysis, solubility and infrared spectra[2] (Fig. 1) were somewhat lower melting and gave depressions of mixture melting points with the substances obtained by sodation of Ia and Ib. The assumption that the pairs IVa and IVb prepared by sodation of Ia and Ib and by irradiation of VIIIa and VIIIb were diastereomers is supported by the recent findings of Gaertner (8) who reports this phenomemon to be common for substituted benzopinacols prepared by different methods. Degradation (9) of both of the diastereomers of IVa to the same benzophenone (VIIIa) gives support to the assumed structure.

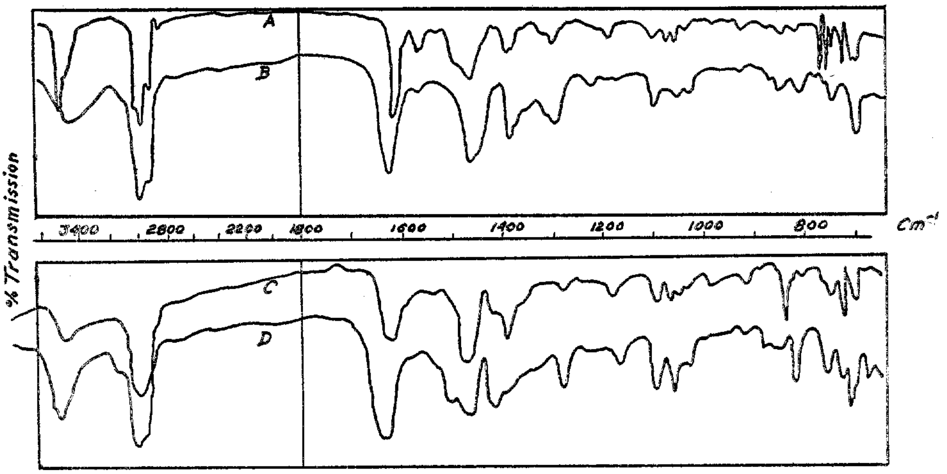

FIG. 1. INFRARED SPECTRA OF *p,p'*-BIS-N,N-(DIALKYLCARBOXAMIDO)BENZOPINACOLS (NUJOL MULLS). Curve A: IVb from the sodation reaction. Curve B: IVb from irradiation. Curve C: IVa from the sodation reaction. Curve D: IVa from irradiation.

A mechanism involving the formation and subsequent reaction of a metal ketyl free radical (A, reaction 1) is proposed to account for the products obtained by the sodation of N,N-dialkylbenzamides. Convincing evidence for a metal ketyl intermediate in the analogous sodation of esters, the acyloin reaction, has been presented by Kharasch (10) and others (11, 12). The fact that aromatic N,N-dialkylamides react with sodium, while the aliphatic analogs do not, may

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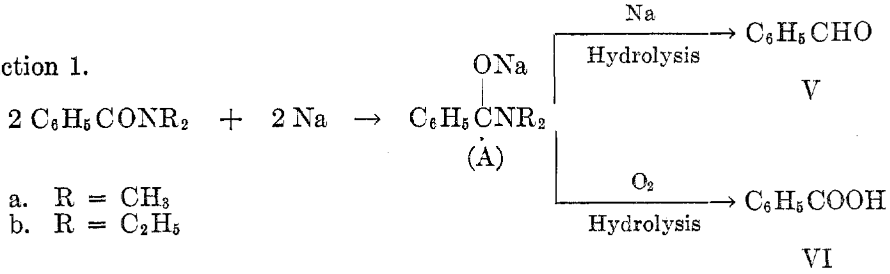
[2] We are indebted to Dr. R. C. Gore of the American Cyanamid Company, Stamford, Connecticut, for the determination of the infrared spectra. The absorption bands at 3000, 1460, and 1380 cm^{-1} are due to the Nujol in which the compounds were mulled.

be accounted for by the lower activation energy required to form the resonance-stabilized aromatic ketyl (A).

Reaction 1.

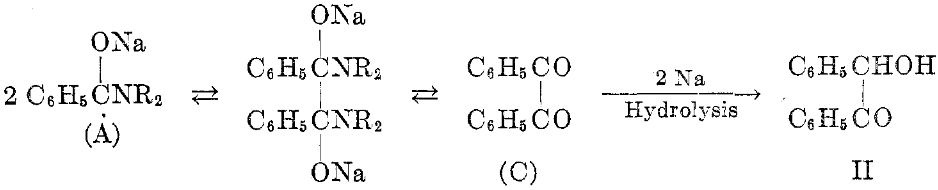


$$2\,C_6H_5CONR_2 + 2\,Na \rightarrow \underset{(A)}{C_6H_5\underset{\cdot}{\overset{\overset{ONa}{|}}{C}}NR_2} \left\{ \begin{array}{l} \xrightarrow[\text{Hydrolysis}]{Na} \underset{V}{C_6H_5CHO} \\ \xrightarrow[\text{Hydrolysis}]{O_2} \underset{VI}{C_6H_5COOH} \end{array} \right.$$

a. $R = CH_3$
b. $R = C_2H_5$

Benzoin (II), the expected product of an acyloin reaction, is indeed obtained by the sodation of Ia, but not from Ib, due probably to steric hindrance which is discussed in detail below. The dimerization (reaction 2) of the ketyl (A) to form benzil (C) by elimination of dimethylsodamide from the dimer and subsequent reduction of benzil to benzoin (II) is entirely analogous to the mechanism preposed for the formation of II by the sodation of ethyl benzoate (10,11).

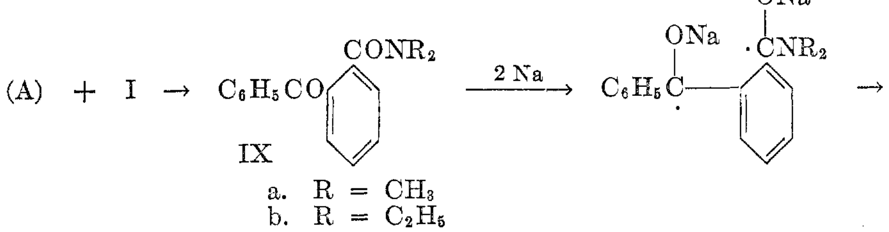
Reaction 2.

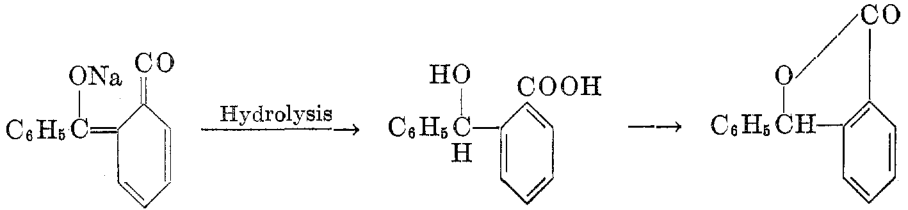


$$2\,\underset{(A)}{C_6H_5\underset{\cdot}{\overset{\overset{ONa}{|}}{C}}NR_2} \rightleftarrows \begin{array}{c} ONa \\ | \\ C_6H_5CNR_2 \\ | \\ C_6H_5CNR_2 \\ | \\ ONa \end{array} \rightleftarrows \underset{(C)}{\begin{array}{c} C_6H_5CO \\ | \\ C_6H_5CO \end{array}} \xrightarrow[\text{Hydrolysis}]{2\,Na} \underset{II}{\begin{array}{c} C_6H_5CHOH \\ | \\ C_6H_5CO \end{array}}$$

It is apparent from the structure of III and VII (reactions 3 and 4) that they were formed by the attack of the carbonyl group of one amide molecule at the *ortho* position of another amide molecule. Such an attack, *ortho* to a *meta*-directing substituent, is common for the reactions of free radicals in aromatic solvents (13). The attack of the free radical (A) at the *ortho* position of the aromatic nucleus of I with elimination of dialkylsodamide would yield the postulated intermediate, 2-N,N-dialkylcarboxamidobenzophenone (IX) (reaction 3). Further reaction of IX with sodium could give rise to phenylphthalide (III) by the reaction sequence shown and to anthraquinone (VII) by the ring closure indicated (reaction 4); this latter product, however, was only isolated from the sodation of Ib.

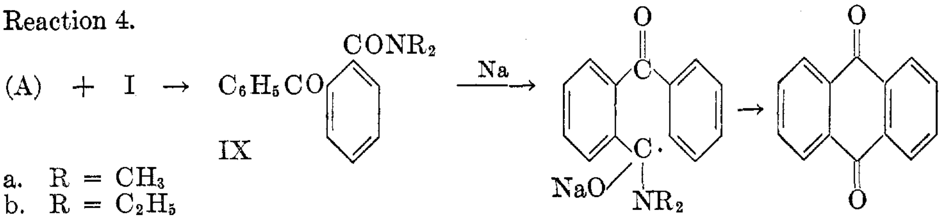
Reaction 3.





III

Reaction 4.



IX

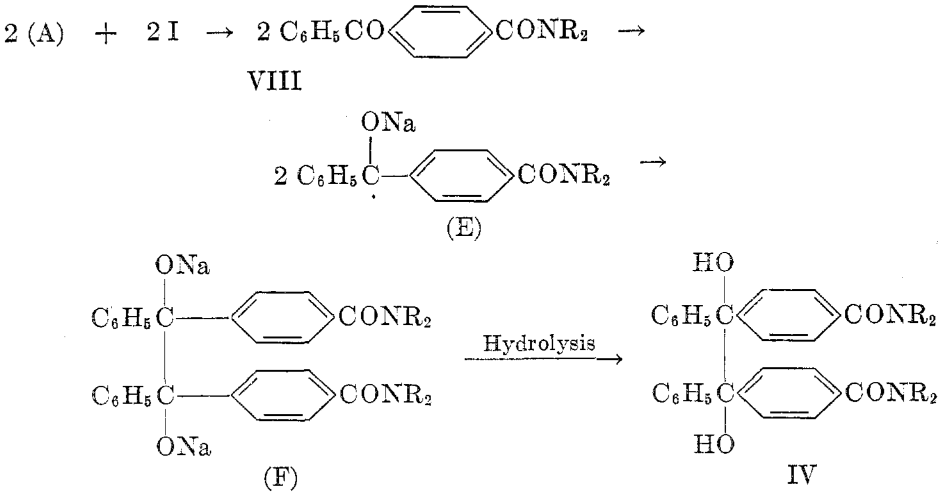
VII

a. R = CH_3
b. R = C_2H_5

The postulated intermediate, IXb, was prepared and reacted with sodium in benzene; both III and VII were obtained, thus lending considerable support to the proposed mechanism. It may be noted that a similar ester, 2-carbethoxybenzophenone, on sodation in benzene yielded only III. The reason for the failure of this ester and of Ia to form anthraquinone (VII) is not apparent at this time.

Attack by the ketyl (A) at the *para* position of I with subsequent elimination of dialkylsodamide should yield the postulated intermediate, VIII, which on sodation would be expected to form the disodium pinacolate (F) by dimerization of the metal ketyl (E).

Reaction 5.



VIII

(E)

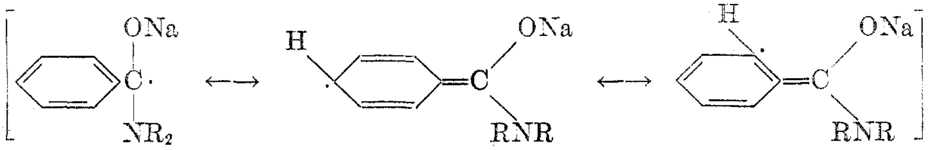
(F)

IV

a. R = CH_3
b. R = C_2H_5

Hydrolysis with acid has been shown to yield benzopinacols from similar systems (3). The very small yield of IV and the failure to isolate it from the products of sodation of VIII indicate its extreme susceptibility to alkaline cleavage. It is significant that such a relatively large yield, 12%, of 4-carboxybenzophenone was obtained by oxidation of the residue from the sodation of Ia. It is probable that the residue contained a considerable amount of a mixture of VIIIa and the corresponding benzohydrol which would be the expected products of an alkaline cleavage of IV (9). Mixtures of this sort have been reported (3) very difficult to separate by ordinary means. Simpler products of the sodations of I [benzaldehyde (V) and benzoic acid (VI)] have been observed as products of the similar reduction of ethyl benzoate (10). The former presumably arising from hydrolysis of the disodium compound (D) and the latter from oxidation and hydrolysis of the metal ketyl (A) (reaction 1).

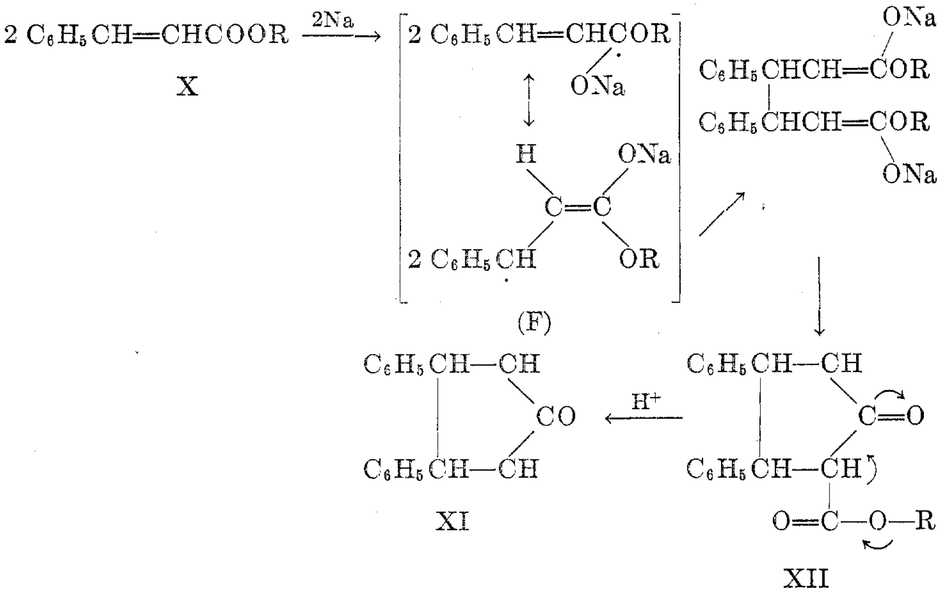
The unexpected course taken by the reaction of N,N-dialkylbenzamides (I) with sodium and the failure to observe any benzoin (II) formation whatsoever from the sodation of Ib may be accounted for by the effect of steric hindrance to head-to-head coupling of the metal ketyl (A) due to the required coplanarity of its resonance hybrid (14). Fischer-Hirschfelder models clearly demonstrate the shielding of the carbonyl carbon atom by the alkyl groups, particularly ethyl, attached to the amide nitrogen.



Experimental evidence to support the above theory was obtained from the reactions of several other similarly hindered systems. The fact that *tert*-butyl benzoate failed to react with sodium even after prolonged heating, while *tert*-butyl propionate reacted quite readily to yield propionoin, is in agreement with expectation. This successful use of an ester other than ethyl or methyl in the acyloin reaction appears not to have been reported previously. Isopropyl benzoate and *n*-butyl benzoate on sodation gave only polymeric material; however, when dilute silfuric acid was added dropwise while stirring immediately following the addition of isopropyl benzoate to a suspension of sodium an 11% yield of benzoin (II) was obtained. This technique has been used successfully by Kapron in the mixed acyloin condensation of an ester-ketone mixture (15). Apparently the steric effect of the isopropyl group does not hinder the reaction to a great extent. Ethyl and *tert*-butyl mesitoate were prepared and reacted with sodium in benzene; however, in neither case was any reaction observed, thus indicating the very hindered nature of these esters.

The esters of cinnamic acid, being vinylogs of the corresponding benzoates, would be expected to behave in an analogous manner. The double bond character of the carbonyl carbon-α-carbon bond due to resonance would require a coplanar structure for the metal ketyl of a cinnamate. The sodation of ethyl cinnamate in xylene has been reported (16) to yield only *cis*- and *trans*-3,4-diphenylcyclopentanone (XI); the expected product, cinnamoin, was not observed. In the present work the sodation of *tert*-butyl cinnamate (X) in benzene was investigated. The previously observed products were isolated as well as the probable precursor, *tert*-butyl 2-oxo-4,5-diphenylcyclopentanecarboxylate (XII), which was characterized by its analysis, formation of its enol-acetate, and decarboxylation to XI. The failure to isolate cinnamoin is in agreement with the expectation that the coplanar nature of the metal ketyl of *tert*-butyl cinnamate would offer steric hindrance to the normal acyloin reaction. The following series of reactions (reaction 6) provides a possible path for the formation of the observed products.

Reaction 6.



The dimerization of the metal ketyl (F) is analogous to the bimolecular reductions of certain α,β-unsaturated ketones (17), in which case ring closures of the 1,6-diketones to cyclopentenes have also been observed. The ready decarboxylation of the *tert*-butyl β-ketoester (XII) may be due to the lability of the alkyl-oxygen bond of the ester, as has been shown by the acid hydrolysis of *tert*-butyl esters (18).

EXPERIMENTAL[3]

General procedure for sodation reactions. All operations were carried out under completely anhydrous conditions while under a slight positive pressure of dry, oxygen-free nitrogen. The reactants were carefully purified and the benzene employed as the reaction solvent was thiophene-free and anhydrous. The required amount of sodium was made into a fine sand in a three-neck flask fitted with a condenser, Herschberg stirrer, nitrogen inlet, and dropping-funnel, by rapidly stirring the molten metal under xylene. The cooled xylene was decanted and the sodium briefly rinsed with benzene before placing it under benzene in

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[3] All boiling and melting points are corrected.

the reaction flask. The system was flushed with nitrogen for one-half hour prior to the dropwise addition of the amide or ester while stirring the warmed mixture. After stirring at the temperature of the refluxing solvent for the desired reaction period the chilled mixture was hydrolyzed by adding a slight excess of 30% sulfuric acid to the flask while maintaining a nitrogen atmosphere. The benzene solution, usually deep yellow, was decanted from the precipitated sodium sulfate and extracted with 20% sodium carbonate to remove the acid fraction, which is always formed to some extent, particularly from the sodation of esters. After drying over sodium sulfate the excess benzene was removed by distillation and the residue was either distilled or worked for solid products.

Reaction of N,N-dimethylbenzamide and sodium. The sodation of 29.8 g. (0.2 mole) of N,N-dimethylbenzamide [b.p. 93–94° (1 mm.)] with 9.2 g. (0.4 atom) of sodium was carried out in the manner described using a reaction time of four hours. During the reaction a marked color change from yellow to red and finally to deep violet occurred, the color disappearing immediately on hydrolysis. The sodium carbonate extract was acidified and the precipitated acids filtered from solution. After digestion of the acids with sodium carbonate an insoluble fraction was removed. Acidification of the filtrate precipitated 1.0 g. (5%) of benzoic acid (m.p. 119–121°); a mixture melting point with an authentic sample showed no depression. The insoluble material was crystallized from dilute ethanol and gave 0.4 g. (2%) of phenylphthalide (III) melting from 113–115°; there was no depression of the melting point on admixture with an authentic sample. Distillation of the neutral fraction yielded several drops of benzaldehyde (2,4-dinitrophenylhydrazine, m.p. 235°), and 5.3 g. (18%) of unreacted N,N-dimethylbenzamide boiling from 77–78° (0.01 mm.). The stillpot residue was taken up in hot ether. The solution when cooled deposited 0.88 g. (3.5%) of *p,p'*-bis-(N,N-dimethylcarboxamido)benzopinacol as a white powder melting from 225–230° (d).

Anal. Calc'd for $C_{32}H_{32}N_2O_4$: C, 75.59; H, 6.29; N, 5.51.

Found: C, 75.53; H, 6.08, N, 5.15.

On standing further crystallization took place in the mother liquor and 1.14 g. (5.5%) of benzoin (m.p. 133–135°) was obtained. A mixture melting point with an authentic sample showed no depression. After removal of the solvent the residual oil from the mother liquor was oxidized with alkaline permanganate according to the procedure described by Randall (19) from which 2.8 g. (12.4%) of 4-carboxybenzophenone was obtained, m.p. 196–199°. A mixture melting point with an authentic sample showed no depression.

Reaction of N,N-diethylbenzamide with sodium. The reaction of 35.4 g. (0.2 mole) of N,N-diethylbenzamide [b.p. 95° (0.5 mm.)] with 9.2 g. (0.4 atom) of sodium was carried out in described manner using a reaction time of from two to three hours in several runs. As in the previous case a marked color change occurred, the mixture finally becoming deep violet. The sodium carbonate extract of the hydrolyzed mixture on acidification yielded from 0.5–1.3 g. (2.6%) of benzoic acid melting at 121°; a mixture melting point with an authentic sample showed no depression. The neutral benzene solution was concentrated whereupon crystallization occurred yielding from 0.5–2.0 g. (2–10%) of anthraquinone as yellow needles melting at 280°, and on admixture with an authentic sample the melting point was unchanged. Further concentration of the neutral filtrate gave a second crystalline fraction which proved to be 1.0 g. (5%) of phenylphthalide melting at 115° after crystallization from dilute ethanol. A mixture melting point with an authentic sample showed no depression. On standing further crystallization took place in the neutral mother liquor which yielded 0.4 g. (1.5%) of *p,p'*-bis(N,N-diethylcarboxamido)benzopinacol as a white, relatively insoluble powder, m.p. 185–190°.

Anal. Calc'd for $C_{36}H_{40}N_2O_4$: C, 76.30; H, 7.41; N, 4.96.

Found: C, 76.51; H, 7.23; N, 4.70.

An attempt to isolate any benzoin which may have been present in the mother liquors as its phenylosazone was unsuccessful.

Proof of structure of p,p'-bis(N,N-dialkylcarboxamido)benzopinacols (IVa and IVb). Infrared analysis clearly indicated hydroxyl group absorption bands at 2450 and 3520 cm^{-1} for IVa and IVb respectively as well as carboxamido bands at 1620 cm^{-1} for IVa and 1615

cm^{-1} for IVb. The hydroxyl groups were shown to be tertiary by unsuccessful attempts to acetylate or oxidize them. A solution of IVb in acetic anhydride containing a few drops of concentrated sulfuric acid was heated for one half hour. No crystalline product could be isolated from the reaction mixture. A solution of IVa and aluminum isopropoxide in an acetone-benzene solution (2) was refluxed for 16 hours with no apparent effect, the starting material being recovered quantitatively. Cleavage of 30 mg. (0.06 (milliequiv.) of *p,p'*-bis-(N,N-dimethylcarboxamido)benzopincol (IVa) by 0.02 milliequiv. of sodium ethoxide in an ether-benzene solution under nitrogen (9) at ambient temperature and subsequent oxidation of the cleavage mixture by refluxing with aluminum isopropoxide in an acetone-benzene solution (2) for 16 hours yielded 3 mg. (10%) of 4-N,N-dimethylcarboxamidobenzophenone melting from 100–103° after crystallization from dilute ethanol. The melting point was unchanged on admixture with an authentic sample.

4-N,N-dimethylcarboxamidobenzophenone (IXa), was prepared in good yield by the reaction of the acid chloride of 4-carboxybenzophenone [m.p. 197–200°, prepared by Wertheim's method (20)] and 25% aqueous dimethylamine. After several crystallizations from dilute ethanol the amide melted at 106°.

Anal. Calc'd for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93; N, 5.53.
Found: 75.60; H, 6.19; N, 5.80.

The *2,4-dinitrophenylhydrazone* of 4-N,N-dimethylcarboxamidobenzophenone after crystallization from ethanol-ethyl acetate melted from 252–255°(d).

Anal. Calc'd for $C_{22}H_{18}N_5O_5$: C, 61.54; H, 4.42; N, 16.32.
Found: C, 61.38; H, 4.58; N, 16.22.

4-N,N-diethylcarboxamidobenzophenone (IXb) was prepared in the manner described above and after crystallization from dilute ethanol melted from 75–76°.

Anal. Calc'd for $C_{18}H_{19}NO_2$: C, 76.87; H, 6.77; N, 4.98.
Found: C, 76.81; H, 6.37; N, 4.89.

4-N,N-dimethylcarboxamidobenzohydrol was prepared by the aluminum isopropoxide reduction (4) of 4-N,N-dimethylcarboxamidobenzophenone in 85% yield as white crystals melting from 78.5–79.5° after crystallization from benzene-petroleum ether.

Anal. Calc'd for $C_{16}H_{17}NO_2$: C, 75.25; H, 6.66; N, 5.48.
Found: C, 75.20; H, 6.71; N, 5.48.

4-N,N-diethylcarboxamidobenzohydrol was obtained in a similar manner and after crystallization from benzene-petroleum ether melted from 67–70°.

Anal. Calc'd for $C_{18}H_{19}NO_2$: N, 4.94. Found: N, 4.95.

p,p'-Bis(N,N-dimethylcarboxamido)benzopinacol (IVa) was obtained in 65% yield by irradiation with ultraviolet light of a propanol-2 solution (7) of 4-N,N-dimethylcarboxamidobenzophenone (VIIIa) for two days. The white crystalline product which separated from the solution melted from 167–177° after many crystallizations from dilute ethanol.

Anal. Calc'd for $C_{32}H_{32}N_2O_4$: C, 75.59, H, 6.29; N, 5.51.
Found: C, 75.77; H, 6.45; N, 5.49.

Infrared analysis: Strong hydroxyl bond at 3500 cm^{-1} and strong carboxamido bond at 1630 cm^{-1} (Fig. 1). A mixture melting point with IVa obtained by the sodation of N,N-dimethylbenzamide (Ia) showed a marked depression; however, a degradation in the manner previously described in the structure proof of IVa obtained by sodation of Ia also yielded 4-N,N-dimethylcarboxamidobenzophenone (VIIIa) in 30% yield melting from 104–106°. A mixture melting point with an authentic sample showed no depression.

p,p'-Bis(N,N-diethylcarboxamido)benzopinacol (IVb) was prepared in 25% yield in a manner identical with that described above. After repeated crystallizations from benzene-petroleum ether and from dilute ethanol the white crystalline product melted from 155–165°.

Anal. Calc'd for $C_{36}H_{40}N_2O_4$: C, 76.59; H, 7.09; N, 4.96.
Found: C, 76.40; H, 7.31; N, 5.35.

Infrared analysis: strong hydroxyl bond at 3400 cm^{-1} and strong carboxamido bond at 1630 cm^{-1} (Fig. 1). A mixture melting point with IVa obtained by the sodation of N,N-diethylbenzamide (Ib) showed a marked depression.

2-N,N-diethylcarboxamidobenzophenone (IXb) was obtained in 73% yield from the reaction of *o*-benzoylbenzoyl chloride and diethylamine in dry benzene. After crystallization from dilute ethanol the white crystalline product was found to melt from 76–77°.

Anal. Calc'd for $C_{18}H_{19}NO_2$: N, 4.98. Found: N, 4.80.

Reaction of 2-N,N-diethylcarboxamidobenzophenone (IX) *with sodium* was carried out in the manner previously described using 25.7 g. (0.1 mole) of IX and 4.6 g. (0.2 atom) of sodium for a reaction period of three hours. The solution turned a very deep blue color during the course of the reaction. On concentration of the neutral benzene fraction from the hydrolyzed mixture 1.1 g. (5.3%) of anthraquinone crystallized as yellow needles melting from 280–281°. Further crystallization occurred on concentration of the mother liquor and 4.9 g. (23%) of phenylphthalide melting at 115° was obtained by filtration. The identity of both products was confirmed by mixed melting points with authentic samples.

Reaction of 2-carbethoxybenzophenone with sodium followed the procedure described using 13.6 g. (0.055 mole) of 2-carbethoxybenzophenone (m.p. 58°, prepared from *o*-benzoylbenzoyl chloride and ethanol in 67% yield) and 9.2 g. (0.4 g.) of sodium for a reaction period of two hours, during which time the mixture turned deep scarlet. From the concentrated neutral fraction only 0.3 g. (2.5%) of phenylphthalide melting from 113–116° was obtained. The bulk of the reaction product was present as neutral polymeric material and a large acid fraction.

Reaction of tert-butyl propionate and sodium was accomplished in the manner described using 13 g. (0.1 mole) of *tert*-butyl propionate [b.p. 118–118.5° (760 mm.), n_D^{20} 1.3937, prepared in 78% yield by Baker's method (21)] and 4.6 g. (0.2 atom) of sodium for a reaction period of three hours. Fractional distillation of the neutral fraction yielded 1.0 g. (20%) of propionoin as a yellow liquid boiling at 42° (3.5 mm.), n_D^{20} 1.4310.

Reaction of isopropyl benzoate and sodium employed a modification of the procedure described using 26.4 g. (0.16 mole) of isopropyl benzoate [b.p. 92–92.5° (10 mm.), n_D^{20} 1.4950; prepared in 89% yield by the method of Norriss (22)] and 7.4 g. (0.32 atom) of sodium. The innovation was the immediate dropwise addition of cold 30% sulfuric acid to the mixture following rapid addition of the ester. The mixture was chilled and stirred while decomposing the sodium during which period the solution turned bright yellow. Distillation of the neutral fraction yielded 18.3 g. (70%) of unreacted starting material and 2.0 g. (11%) of benzoin, melting from 134–136°, was obtained by crystallization of the residue.

Reaction of tert-butyl cinnamate with sodium was accomplished in the manner described using 20 g. (0.1 mole) of *tert*-butyl cinnamate [b.p. 108° (1 mm.), n_D^{20} 1.5373, prepared by Baker's method (21)] and 4.6 g. (0.2 atom) of sodium for a reaction period of 16 hours. On concentration of the neutral fraction there was obtained 2.4 g. (14%) of *tert*-butyl 2-oxo-4,5-diphenylcyclopentanecarboxylate as colorless needles melting from 165–168° after crystallization from benzene-petroleum ether.

Anal. Calc'd for $C_{22}H_{24}O_3$: C, 78.60; H, 7.11.
Found: C, 78.57; H, 7.11.

The enol-acetate was prepared by warming the compound with acetic anhydride in pyridine. After crystallization from methanol the colorless crystals melted from 76–77°.

Anal. Calc'd for $C_{24}H_{26}O_4$: C, 76.18; H, 6.88.
Found: C, 76.04; H, 6.88.

An attempted crystallization of *tert*-butyl 2-oxo-3-4-diphenylcyclopentanecarboxylate from ethanol resulted in decarboxylation to *trans*-3,4-diphenylcyclopentanone melting at 177–179°. Also the product obtained by warming *tert*-butyl 2-oxo-3,4-diphenyl-cyclopentanecarboxylate with an acidic solution of 2,4-dinitrophenylhydrazine was found to be the derivative of *trans*-3,4-diphenylcyclopentanone, melting at 173°. The identity of both decarboxylation products was confirmed by their melting points and analyses. The neutral mother liquor was distilled under a high vacuum and the distillate sodified on cooling. Fractional crystallization from petroleum ether yielded two colorless crystalline products: *cis*-3,4-diphenylcyclopentanone melting from 102–105° (15)

Anal. Calc'd for $C_{17}H_{16}O$: C, 86.50; H, 6.77.
Found: C, 86.35; H, 6.82.

The *2,4-dinitrophenylhydrazone* melted from 205–206° after crystallization from ethyl acetate; reported m.p. 208° (23),

Anal. Calc'd for $C_{23}H_{20}N_4O_4$: C, 66.30; H, 4.80; N, 13.50.
Found: C, 66.08; H, 5.03; N, 13.38.

and *trans*-3,4-diphenylcyclopentanone melting from 177–179°; reported m.p. 177° (15).

Anal. Calc'd for $C_{17}H_{16}O$: C, 86.50; H, 6.77.
Found: C, 86.84; H, 6.64.

The *2,4-dinitrophenylhydrazone* was found to melt at 173° after crystallization from ethyl acetate; reported m.p. 170° (23).

Anal. Calc'd for $C_{23}H_{20}N_4O_4$: C, 66.30; H, 4.81; N, 13.52.
Found: C, 66.16; H, 5.18; N, 13.68.

SUMMARY

The reaction of N,N-dialkylbenzamides with sodium yielded a variety of products other than the expected product, benzoin. A mechanism involving the attack of a metal ketyl radical on the aromatic nucleus of the amide is postulated to account for these products and experimental support for this mechanism is offered. The role of steric hindrance in governing the course of this reaction is discussed and demonstrated in several other similarly hindered systems.

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