was used in the case of the butyl compound. The amines all form heavy, pale yellow needles.

N-ALKYL-9-PHENANTHRYLAMINES

Alkyl group	Yield, %	M. p., °C.	% C Calcd.	% C Found	% H Calcd.	% H Found
Methyl	70	88.5–89.5	86.91	86.85	6.33	6.27
Ethyl	70	97 – 98	86.87	86.96	6.84	7.11
n-Propyl	70	109.5–110.5	86.76	86.61	7.29	7.09
n-Butyl	62	102 –103	86.69	86.52	7.69	7.51

N-(β-Hydroxyethyl)-9-phenanthrylamine.—After heating a mixture of 2 g. of 9-phenanthrylamine, 5 cc. of benzene and 10 cc. of ethylene oxide in a sealed tube at 100° for seven hours, the excess ethylene oxide was expelled and the residue was extracted with ether. The solution was dried, decolorized and treated with petroleum ether, when 0.25 g. (10%) of a solid was obtained in the form of fine needles melting at 99.5–101°. The substance has a tendency to separate in a gelatinous condition. After two recrystallizations from ether–petroleum ether it was obtained as long, slender, colorless needles, m. p. 101–102°.

Anal. Calcd. for $C_{16}H_{15}ON$: C, 80.97; H, 6.38. Found: C, 81.22; H, 6.34.

When the reaction mixture was heated at 100° for only five hours considerable 9-phenanthrylamine was recovered along with some of the β-ethanol derivative. On conducting the reaction at 135–140° for either ten or twenty hours the ethereal extract of the product yielded only a resinous residue on evaporation. This distilled without apparent decomposition at about 250° (2 mm.) but the viscous, pale yellow distillate set to a glass and did not crystallize.

Summary

Treated with bromine in methyl alcoholic solution, phenanthrene is converted in about 70% yield into a very unstable substance which appears to be a complex containing one molecule each of phenanthrene methoxybromide and phenanthrene dibromide. The complex yields 9-methoxyphenanthrene and phenanthrene when warmed with alcoholic potassium hydroxide–acetate, and 9-phenanthrol is easily obtained from the mixture in a sufficiently satisfactory over-all yield to make this a useful preparative method. 9-Phenanthrylamine and typical N-alkyl derivatives can be obtained in good yield from 9-phenanthrol by the Bucherer reaction.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS. RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Acylation and Alkylation of Beta Diketones and Beta Sulfonyl Ketones

BY E. P. KOHLER AND H. A. POTTER

In a recent paper,[1] in which we described the action of benzoyl chloride on the magnesium derivatives of a series of monoketones, we showed that there is a conspicuous difference in the behavior of phenyl and mesitylenic ketones, the former being converted into diketones and the latter largely into benzoates. We have now extended the comparison to the corresponding β-diketones and, as these diketones form copper derivatives which can be purified by crystallization, we were able to compare the behavior of phenyl and mesitylenic ketones when they are benzoylated by means of metallic derivatives that are very different from the magnesium compounds in their activity.

We also included in the comparison the corresponding β-sulfonyl ketones—tosyl acetophenone and tosyl acetomesitylene. These compounds are of special interest because the sulfonyl group increases the acidity of the hydrogen on an adjoining carbon atom but is incapable of participating in any process akin to enolization.

The nature of the products and the yields in which they were obtained are shown in the following table. In many cases the primary benzoylation products deprived some of the initial metallic derivatives of their metal and thus prevented complete acylation; the proportion of C-benzoyl to O-benzoyl derivatives is therefore more significant than the total yield. In the case of the copper compounds the great differences in solubility introduce an additional complication because in the very slow reactions a part of the initial material is lost through halogenation by the mechanism recently established by Michael and Carlson.[2] An attempt to obviate this difficulty by substituting benzoyl bromide for the chloride—in the cases marked with an asterisk—was unsuccessful because, while the bromide reacts far more rapidly than the chloride, the resulting cupric bromide is also a much better halogenating agent than the chloride.

An examination of this table shows that the difference in the mode of benzoylation of phenyl

(1) Kohler, Tishler and Potter, THIS JOURNAL, 57, 2517 (1935).

(2) Michael and Carlson, *ibid.*, 58, 353 (1936).

TABLE I

Substance	Product	C-Acylation Per cent.	Product	O-Acylation Per cent.
$[(C_6H_5CO)_2CH]MgX$	$(C_6H_5CO)_3CH$	80.5	.....	0
$[(C_6H_5CO)_2CH]_2Cu$	$(C_6H_5CO)_3CH$	80	.....	0
$[(C_6H_5CO)_2CH]_2Cu$*	$(C_6H_5CO)_3CH$	60	$(C_6H_5C(OCOC_6H_5)=CHCOC_6H_5$ (I)	22
$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]MgX$	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	65	$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]COC_6H_5$ (II)	18
$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]_2Cu$	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	60	$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]COC_6H_5$ (II)	30
$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]_2Cu$*	$(C_6H_5CO)_2CHCOC_6H_2(CH_3)_3$	45	$[(C_6H_5CO)(C_6H_2(CH_3)_3CO)CH]COC_6H_5$ (II)	30
$[(C_6H_2(CH_3)_3CO)_2CH]MgX$	.....	0	$(CH_3)_3C_6H_2C(OCOC_6H_5)=CHCOC_6H_2(CH_3)_3$ (III)	96
$[(C_6H_2(CH_3)_3CO)_2CH]_2Cu$	.....	0	$(CH_3)_3C_6H_2C(OCOC_6H_5)=CHCOC_6H_2(CH_3)_3$ (III)	49
$[(C_7H_7SO_2)(C_6H_5CO)CH]MgX$	$C_7H_7SO_2CH(COC_6H_5)_2$ (IV)	81	.....	0
$[(C_7H_7SO_2)(C_6H_2(CH_3)_3CO)CH]MgX$	$C_7H_7SO_2CH(COC_6H_5)C_6H_2(CH_3)_3$ (V)	16	$C_7H_7SO_2CH=C(OCOC_6H_5)C_6H_2(CH_3)_3$	64
$[(C_7H_7SO_2)_2CH]MgX$	$(C_7H_7SO_2)_2CHCOC_6H_5$	80	.....	0
$[(C_7H_7SO_2)(C_6H_5CO)_2C]MgX$	.....	0	$C_7H_7SO_2C(C_6H_5CO)=C(OCOC_6H_5)C_6H_5$ (VII)	96
$[(C_7H_7SO_2)_2(C_6H_5CO)C]MgX$	.....	0	$(C_7H_7SO_2)_2C=C(OCOC_6H_5)C_6H_5$ (VIII)	
$[(C_6H_5SO_2)_2CH]MgX$	$(C_6H_5SO_2)_2CHCOC_6H_2(CH_3)_3$ (IX)	80	.....	0

and mesitylenic ketones is just as marked in the β-diketones and the β-sulfonyl ketones as it is in the monoketones. It shows also that the course of the benzoylation of the metallic derivatives of these compounds is not greatly affected by the nature of the metal; it depends almost entirely on the character of the hydrocarbon residues and the mesityl group effectively promotes O-benzoylation.

For reasons stated earlier, the β-sulfonyl ketones are especially interesting. As they behaved toward benzoylating agents essentially like the polyketones, we also examined the behavior of tosyl acetomesitylene in reactions involving alkylation. In alcohol the sodium compound reacted rapidly with methyl iodide and the sole product of the reaction was the C-alkyl derivative. We were unable to induce either the magnesium or the sodium compound to react with methyl iodide in ether or benzene but both reacted with dimethyl sulfate in these non-polar solvents and formed O-methyl derivatives exclusively. Mesitylenic ketones, therefore, differ from phenyl ketones also in their tendency to form O-alkyl derivatives.

These β-sulfonyl ketones also provided a means of examining the view that sulfonyl groups do not promote the enolization of a carbonyl group in the β-position because they cannot serve as partners in conjugation. In support of this view Arndt and Martius[3] described the behavior of a series of mono- and disulfonyl compounds toward alcoholic ferric chloride. The behavior of our series of sulfonyl compounds in solutions of ferric chloride in methyl alcohol—or better in freshly prepared solutions in acetone—was as follows: with $C_7H_7SO_2CH_2COC_6H_5$, $C_7H_7SO_2CH_2COC_6H_2(CH_3)_3$ and $(C_7H_7SO_2)_2CHCOC_6H_5$ the tests were negative; $C_7H_7SO_2CH(COC_6H_5)_2$ slowly developed a red color which was feeble in alcohol, stronger in acetone; both $C_7H_7SO_2CH(COC_6H_5)COC_6H_2(CH_3)_3$ and $(C_6H_5SO_2)_2CHCOC_6H_2(CH_3)_3$ rapidly developed deep red colors in both solvents.

(3) Arndt and Martius, *Ann.*, **499**, 244 (1932).

The view that sulfonyl groups cannot promote enolization is manifestly no longer tenable because the difference between acetomesitylene which does not respond to any tests for enolization and disulfonyl derivative which enolizes must be due to the two phenylsulfonyl groups. It is doubtless true that the sulfonyl group is far less effective than the carbonyl group in promoting enolization; the introduction of another benzoyl group into the completely enolic dibenzoylmethane merely stabilizes the ketonic form while the introduction of a tosyl group completely inhibits enolization. But when the same group is introduced into benzoyl acetomesitylene, the product still enolizes in solution—an indication that the tendency to enolize is much more pronounced in mesitylenic than in phenyl ketones.

From the foregoing account and the facts presented in the earlier paper it is evident that all types of ketones which contain the group CH–$COC_6H_2(CH_3)_3$ differ from those which have the group CH–COC_6H_5 in that they have a greater tendency to enolize and to form acyl and alkyl derivatives of the enolic modification. The reason for this peculiarity is not clear but it appears probable that the predominant O-acylation and O-alkylation is associated with the tendency to enolize.

Experimental Part

I. Preparation of Materials

The diketones and their copper derivatives which were known were prepared by conventional methods but the copper derivative of dibenzoylmethane was recrystallized before use by solution in pyridine and reprecipitation with ether. Tosyl acetophenone was made by Arndt and Martius[3] (p. 281) by treating chloroacetophenone with sodium toluene sulfinate. In order to secure the intermediates, we undertook to prepare it by means of a series of reactions which can be represented as follows

$$C_7H_7SNa + ClCH_2COC_6H_5 \longrightarrow C_7H_7SCH_2COC_6H_5 \longrightarrow C_7H_7SOCH_2COC_6H_5 \longrightarrow C_7H_7SO_2CH_2COC_6H_5$$

We found, however, that, owing to oxidation and reduction in the alkaline solution, the principal products of the first step were the sulfoxide and acetophenone. The procedure was as follows.

A solution of 172 g. of chloroacetophenone in boiling methyl alcohol was treated with an equivalent quantity of sodium *p*-thiocresolate. The mixture was boiled for several hours, then freed from most of the methyl alcohol by distillation. An ethereal extract of the residue, distilled under diminished pressure, gave 50 g. of acetophenone and 168 g. of the sulfoxide. The sulfoxide melts at 46° and boils at 182–184° (5 mm.). It is oxidized to the sulfone by hydrogen peroxide.

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.7; H, 5.6. Found: C, 69.6; H, 6.0.

Tosyl Acetomesitylene: $C_7H_7SO_2CH_2COC_6H_2(CH_3)_3$.—Sodium toluene sulfinate reacts much less readily with chloroacetomesitylene than with chloroacetophenone. The best results were obtained by heating equivalent quantities of the reactants and a small quantity of alcohol (about one-third of the volume of the solids) in sealed tubes for seventy-five hours at 100°. The contents of the tubes were acidified with dilute acid and extracted with benzene. The benzene solution, in turn, was extracted with bicarbonate to remove sulfinic acid and finally with normal aqueous sodium hydroxide. From the yellow alkaline solution acids precipitated the sulfonyl ketone. It crystallized from methyl alcohol in needles and it melted at 180°. The yield was about 50%.

Anal. Calcd. for $C_{18}H_{20}O_3S$: C, 68.4; H, 6.3. Found: C, 68.2; H, 6.3.

Tribenzoyl Methyl Chloride: $(C_6H_5CO)_3CCl$.—A slow stream of chlorine was passed through a suspension of tribenzoylmethane until all of the solid disappeared. The chloroform was evaporated and the residue was recrystallized from methyl alcohol. The product separated in needles melting at 122°.

Anal. Calcd. for $C_{22}H_{15}O_3Cl$: C, 72.8; H, 4.1. Found: C, 72.5; H, 4.2.

The chloride did not serve the purpose for which it was made because sodium toluene sulfinate reduced it rapidly and quantitatively to tribenzoylmethane and when it was treated with sodium thiocresolate in benzene it reacted in accordance with the equation

$$(C_6H_5CO)_3CCl + 2NaSC_7H_7 \longrightarrow NaCl + (C_6H_5CO)_3CNa + C_7H_7S—SC_7H_7$$

II. Benzoylation

In order to get significant results with the magnesium derivatives it was necessary to prepare and benzoylate them in ether at low temperatures because at higher temperatures both the magnesium derivatives themselves and their benzoylation products are cleaved in part into new magnesium derivatives which then undergo further benzoylation. Thus when the magnesium derivative of benzoyl acetomesitylene was benzoylated in boiling benzene the principal products were the magnesium derivatives of dibenzoyl and tribenzoyl methane.

For manifest reasons some diketone or sulfo ketone was regenerated in all cases in which one of the products was formed by C-benzoylation. In many of these cases also—especially in the benzoylation of the sulfonyl compounds—the primary product suffered further benzoylation. The final result, therefore, was a mixture which might contain diketone and one or more of its stereoisomeric benzoates, triketone and its benzoates, and the excess of acid chloride. And, in the case of the copper compounds, usually it also contained a halogen derivative of the diketone.

The separation of these mixtures, frequently troublesome, was in part chemical. In general ether, when present, was removed and replaced with benzene. The benzene solutions were boiled with water to decompose excess of chloride or bromide, then cooled and extracted with dilute bicarbonate until free from benzoic acid. The benzene layer was then shaken with sodium carbonate which converted a part of the triketone into the sparingly soluble ketonic modification and removed the remainder as a solu-

ble sodium salt. Extraction with aqueous sodium hydroxide then removed both the regenerated diketone and its halogen compound and these substances were separated either by crystallization or when necessary by converting the diketone into its copper derivative. The benzene solution then contained only benzoates. The separation of the isomeric benzoates by crystallization was always troublesome and sometimes impossible but the nature of the products and the quantities in which they were present could always be established by hydrolysis with cold dilute methyl alcoholic sodium hydroxide. The important constants of the new products are recorded in the following table. The Roman numerals refer to structural formulas in Table I.

TABLE II

Formula	Crystal form	M. p., °C.	Composition, % Calcd. C	Calcd. H	Found C	Found H
$C_{22}H_{16}O_3$ (I)	(a) Yellow tables	108	80.5	4.8	80.3	4.9
	(b) Colorless cubes	125	80.5	4.8	80.2	4.8
$C_{25}H_{22}O_3$ (II)	Yellow prisms	91	81.1	6.0	81.0	6.3
$C_{28}H_{28}O_3$ (III)	Yellow plates	136	81.6	6.8	81.5	6.8
$C_{22}H_{18}O_4S$ (IV)	Thin needles	196	69.8	4.8	69.6	4.5
$C_{25}H_{24}O_4S$ (V)	Prisms	147	71.4	5.7	71.2	5.7
$C_{25}H_{24}O_4S$ (VI)	(a) Needles	120	71.4	5.7	71.4	5.8
	(b) Prisms	126	71.4	5.7	71.6	5.7
$C_{29}H_{22}O_5S$ (VII)	Needles	166	72.2	4.6	72.1	4.6
$C_{29}H_{21}O_5BrS$ (VIII)	Prisms	189	62.0	3.7	61.7	3.8
$C_{22}H_{17}O_4BrS$ (IX)	Needles	212	57.8	3.7	58.1	3.9
$C_{29}H_{21}O_5BrS$ (X)	(a) Needles	182	62.0	3.7	61.9	3.9
	(b) Prisms	201	62.0	3.7	61.8	4.0

III. Proof of Structure

In most cases the products formed by O-acylation were readily distinguished from the C-acyl derivatives by their lack of solubility in aqueous alkali. This test, however, was not applicable to those tosyl compounds which contained four acyl groups. There was little doubt concerning the structure of these compounds because they were readily formed also by benzoylation in pyridine but we nevertheless decided to establish with certainty the manner in which the fourth acyl group enters the molecule. To this end we employed *p*-bromobenzoyl chloride in accordance with the scheme

$C_7H_7SO_2CH_2COC_6H_5 \longrightarrow C_7H_7SO_2CH(COC_6H_5)_2 \longrightarrow [C_7H_7SO_2C(COC_6H_5)_2]COC_6H_4Br$

VIII

$C_7H_7SO_2CHCOC_6H_5 \longrightarrow C_7H_7SO_2CH(COC_6H_4Br)COC_6H_5 \longrightarrow$

IX

$[C_7H_7SO_2C(COC_6H_4Br)COC_6H_5]COC_6H_5$

X

As the final products of the two series are different, the fourth group evidently enters as benzoate. The constants of these compounds have been included in Table II.

IV. Alkylation of Tosylacetomesitylene

Alkylation with Diazomethane: $C_7H_7SO_2CH{=}C(OCH_3)$-$C_6H_2(CH_3)_3$.—An excess of diazomethane was passed into a solution of the sulfonyl ketone in cold benzene. The solution evolved gas slowly but regularly. It was left to itself overnight, then diluted with petroleum ether. The product crystallized from benzene–petroleum ether in large prisms and it melted at 137°. The yield was 93%.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.2; H, 6.8.

This product is evidently an ether because it is insoluble in alkalies and regenerates the sulfonyl ketone when it is digested with hydrochloric acid. When it was heated for six hours to 130° in a vacuum it was transformed into an isomer which crystallized from methyl alcohol in sparkling cubes and melted at 147°. This isomer likewise is an ether; it also is insoluble in alkalies but is hydrolyzed by acids. Neither of these ethers was rearranged to the C-methyl derivative by prolonged boiling with alcoholic sodium methylate.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.0; H, 6.7.

Alkylation of the Magnesium Derivative.—A solution of 6.3 g. of the tosyl compound in benzene was added to a small excess of ethylmagnesium bromide and the solution was distilled until all of the excess ethyl bromide and the ether had been expelled. It was then treated cautiously with excess of dimethyl sulfate, boiled for seven hours and decomposed in the usual manner. The benzene layer contained 6.2 g. of the methyl ether melting at 147°—a yield of 94%.

Alkylation of the Sodium Derivative in Benzene.—A solution of 3.2 g. of the tosyl compound in benzene was treated with an equivalent quantity of sodium and left to itself until all of the metal had disappeared. Excess of dimethyl sulfate was added then and the mixture was boiled for four hours and decomposed in the usual manner. The benzene layer contained 3 g. of the methyl ether melting at 137°—a yield of 90%.

Alkylation with Methyl Iodide in Alcohol: $C_7H_7SO_2CH$-$(CH_3)COC_6H_2(CH_3)_3$.—A boiling methyl alcoholic solution of 3.2 g. of the tosyl compound and 3 g. of methyl iodide was treated gradually with two equivalents of sodium methylate and boiled for two hours. The solution remained clear until it was diluted with ice water. It then deposited a very sparingly soluble product which was recrystallized from acetone–methyl alcohol. It separated in lustrous needles melting at 171°. The yield was 96%.

Anal. Calcd. for $C_{19}H_{22}O_3S$: C, 69.1; H, 6.7. Found: C, 69.2; H, 6.9.

The methyl derivative is extracted from its ethereal solu-

tion by aqueous sodium hydroxide and although very slightly soluble in methyl alcohol it dissolves freely in methyl alcoholic sodium hydroxide. The crude product contained no material that was not extracted from ether by aqueous sodium hydroxide; it therefore contained neither ethers nor dimethyl derivatives.

Summary

This paper contains an account of the results obtained in a study of the acylation and alkylation of a series of β-diketones and β-sulfonyl ketones.

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[CONTRIBUTION NO. 32 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reduction of Nitroguanidine. VII. Preparation of Aminoguanidine by Catalytic Hydrogenation

BY EUGENE LIEBER AND G. B. L. SMITH

The catalytic hydrogenation of nitroguanidine to nitrosoguanidine with nickel and platinum catalysts in neutral media has been reported.[1] The further reduction to aminoguanidine has not been studied extensively.[2] Recently McGill[3] has suggested the manufacture of aminoguanidine by catalytic hydrogenation with a catalyst of nickel dispersed on kieselguhr (all of the ordinary hydrogenating catalysts are also claimed) at temperatures between 25 and 125° (the preferred temperature is 80°) in the *absence* of any substantial amounts of acid. However, it has been found that the optimum conversion to aminoguanidine is obtained in media of relatively high acid concentration. McGill,[3] in the examples cited in the patent, gives no yields but claims that for nickel catalyst the use of elevated pressure is essential for increased yields. We have found that the yields for a nickel catalyst are conditioned not solely by pressure but by the type of solvent used.

The molar ratio of hydrogen to hydrogen acceptor obtained in the catalytic hydrogenation of nitroguanidine depends upon the environmental conditions of the solvent. For the first molar proportion of hydrogen the reduction proceeds as follows.

Media	Principal product	Ratio, H_2 : Acceptor
Neutral	Nitrosoguanidine	1:1
Basic	Nitrosoguanidine	1:1
Acid	Aminoguanidine	3:1

In acid media of such a concentration that the molar ratio of nitroguanidine to acid is one or higher the reduction proceeds without the formation of nitrosoguanidine. This is a new observation and is of significant importance for the preparation of aminoguanidine by catalytic hydrogenation. If the molar ratio of acid to nitroguanidine be below one then the distribution of reduction products depends upon the acid concentration. At ratios of acid above one, the hydrazino formation was found to be linear with hydrogen absorption.

Raney nickel catalyst can be used in both neutral and alkaline media. The Adams platinum oxide catalyst can be used in neutral and acid media but is completely poisoned in alkaline media of even low concentrations. The reduction in neutral aqueous media at atmospheric pressure and room temperature gives low yields of aminoguanidine, the principal products appearing to be ammonia and guanidine. At higher hydrogen pressures superior yields of aminoguanidine are obtained with platinum oxide in 15% aqueous acetic acid as compared with Raney nickel in neutral solvents. With increasing temperatures to 125° the yields of aminoguanidine with Raney nickel fall off more rapidly than with platninum oxide as shown by Fig. 1. This also illustrates the effect of type of solvent, especially at 75°.[3]

Experimental

Method.—The Adams platinum oxide and Raney nickel catalysts were prepared in the usual manner. The apparatus employed has been described previously,[1] while the high pressure equipment was of the Adkins type.

The experimental technique and procedures devised for the recovery of the aminoguanidine with minimum loss will be made clear by the description of typical reductions obtained with platinum and nickel catalysts.

Reduction in Acid Media with Platinum Oxide Catalyst.—20.8 g. of nitroguanidine and 1 g. of platinum oxide are suspended in 125 ml. of 15% aqueous acetic acid. The reduction is carried out at 125 atm. and room temperature

(1) Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

(2) Audrieth and Schmidt, University of Illinois, private communication, used Raney nickel in ethyl alcohol and identified the aminoguanidine through the melting point of the benzalazine obtained by hydrolysis of the reduction mixture.

(3) McGill, U. S. Patent 2,033,203, March 10, 1936.