funnel, washed with water, and dried. Recrystallization from hexane gave 12.1 g. (76%) of copper colored plates of oxime VIII, m.p. 91–93°.

Anal. Calcd. for $C_{11}H_{11}NOFe$: C, 57.67; H, 4.84; N, 6.12; Fe, 24.38. Found: C, 57.81; H, 4.97; N, 6.19; Fe, 24.29.

A 5-g. sample of oxime VIII was added to 5 ml. of acetic anhydride cooled in an ice bath, and the deep red solution was allowed to stand in the refrigerator overnight.[19] To the cold solution was added 50 ml. of 95% ethanol and a little water to give, on scratching, 4 g. of crystals, m.p. 73–76°. Several recrystallizations from hexane gave orange plates of oxime acetate XIII, m.p. 80–81°.

Anal. Calcd. for $C_{13}H_{13}O_2NFe$: C, 57.59; H, 4.83; N, 5.17; Fe, 20.60. Found: C, 57.89; H, 4.79; N, 5.09; Fe, 20.29.

Formylferrocene semicarbazone (IX). This compound was obtained from a 1-gram sample of crude aldehyde VII, semicarbazide hydrochloride and sodium acetate in ethanol-water solution. Recrystallization of the product from 95% ethanol gave orange flakes, m.p. 217–219° dec.

Anal. Calcd. for $C_{12}H_{13}N_3OFe$: C, 53.16; H, 4.83; N, 15.50; Fe, 20.60. Found: C, 53.38; H, 5.07; N, 15.5; Fe, 20.79.

DURHAM, N. C.

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[19] See C. R. Hauser and C. T. Sullivan, *J. Am. Chem. Soc.*, **55**, 4611 (1933).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

Quaternary Hydrazones and Their Rearrangement

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The dimethylhydrazones of several aliphatic and aromatic ketones were prepared, and converted into methiodides which yielded *N,N,N*-trimethylhydrazinium iodide on hydrolysis. The quaternary hydrazones would not undergo a Beckmann type of rearrangement on heating alone, but with sodium ethoxide the Neber variant occurred on compounds having α-hydrogens. The molecular refractions of the dimethylhydrazones and the spectral characteristics of them and their methiodides are reported.

The chemistry of arylhydrazones and to some extent of acylhydrazones has been well developed, but that of alkylhydrazones has been largely neglected, perhaps due in part to the difficult accessibility of alkylhydrazines. The isoelectronic relationship between hydrazones and oximes has led to the speculation that the rearrangements known for oximes should find their parallels with hydrazones. Such rearrangements are characterized by the loss from nitrogen of a species which is the conjugate base of a fairly strong acid, e.g., benzenesulfonate ion. Quaternary hydrazones (I) having three groups on the terminal nitrogen atom might by parallel behavior lose a molecule of tertiary amine, which would satisfy the foregoing characterization

$$R_2C{=}N{-}\overset{+}{N}R_3'X^-$$

I

insofar as the conjugate tertiary ammonium ion is a strong enough acid. The present work was undertaken to elucidate some of the chemistry of alkylhydrazones, with particular attention to the possibility of rearrangements.

Initial attempts to prepare quaternary hydrazones of structure I by reaction of carbonyl compounds with *N,N,N*-trimethylhydrazinium iodide did not succeed. This is not astonishing when one considers the positive charge of the hydrazinium ion and its repulsion for the positive field of the carbonyl carbon atom.

Attention was then turned to N,N-disubstituted hydrazones, which in principle might be further alkylated to quaternary derivatives at either nitrogen. In order to favor terminal alkylation, dimethylhydrazones were chosen, since methyl groups should offer near minimal steric hindrance, and should not decrease the basicity of the terminal nitrogen atom. The preparation of certain dimethylhydrazones from carbonyl compounds and dimethylhydrazine has been reported recently;[2] we were able to repeat and extend the observations reported. Dimethylhydrazine does not react with ketones with the facility shown by aryl- and acyl-hydrazones. This difference is presumably due to the much greater basic strength of dialkylhydrazines, which should reside in the substituted nitrogen atom, a site incapable of hydrazone formation. Furthermore, the simultaneous occurrence of significant concentrations of the free hydrazine and the conjugate acid of the ketone becomes more difficult in proportion to the basic strength of the hydrazine, and it is these two species which appear to react in the rate-determining step of hydrazone formation.[3] We were successful in overcoming the inherent difficulties by using excess anhydrous dimethylhydrazine, at reflux temperatures or in sealed tubes, as the situation warranted. An alternative route to

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[1] From the doctoral thesis of E. E. Most, Jr., whose present address is E. I. du Pont de Nemours and Co., Kinston, Va.

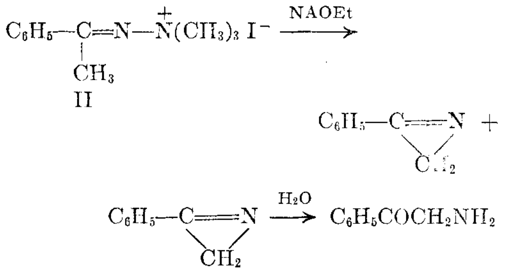
[2] D. Todd, *J. Am. Chem. Soc.* **71**, 1353 (1949).

[3] J. B. Conant and P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2881 (1932); *cf.* E. R. Alexander, *Principles of Ionic Organic Reactions*, John Wiley and Sons, Inc., New York, 1950, pp. 154–165.

dialkylhydrazones, using *gem*-dichlorides in place of ketones, has subsequently been reported.[4]

The dimethylhydrazones of both aliphatic and aromatic ketones readily gave crystalline methiodides. They could be hydrolyzed to *N,N,N*-trimethylhydrazinium iodide, which showed that methylation had occurred on the terminal nitrogen. When heated by themselves, these methiodides were unchanged until a deep-seated decomposition took place; from the tarry residues no pure organic compounds could be isolated. Heating in refluxing ethanol failed to affect the quaternary hydrazone of even dianisyl ketone, which should have been an exceptionally favorable case in view of Chapman and Fidler's determination that the anisyl group migrates in the Beckmann rearrangement more readily than any other group studied.[5] Apparently trimethylamine is too nucleophilic a group to be expelled under the attempted rearrangement conditions, which is not surprising in view of the behavior of similarly placed nucleophilic groups in the Beckmann rearrangement. Chapman and Fidler[5] have shown that *O*-benzoyl- and *O*-2,4-dinitrophenylbenzophenone oximes rearrange at extremely slow rates, and both benzoic acid and 2,4-dinitrophenol are stronger acids than trimethylammonium ion. An attempt to prepare an *N,N*-dimethyl-*N*-picryl quaternary hydrazone by reaction of benzophenone dimethylhydrazone with picryl chloride failed.

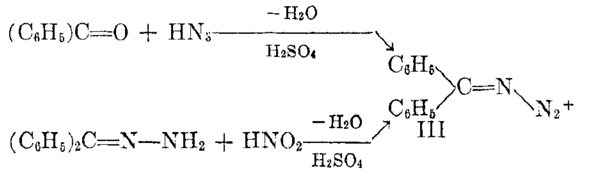
The base-catalyzed oxime rearrangement discovered by Neber[6] occurs when *O*-arylsulfonylketoximes having an α-methylene group are treated with alcoholic alkali; the apparently intermediate azirenes subsequently appear as α-aminoketones or as pyrazines. Under similar conditions, quaternary hydrazones are hydrolyzed instead, and aldol condensation products are formed together with hydrazinium salts. Under strictly anhydrous conditions, with sodium ethoxide in boiling ethanol a rearrangement analogous to the Neber reaction can be induced. Thus acetophenone dimethylhydrazone methiodide (II) gave phenacylamine and trimethylamine. The necessity for strict exclusion of water was shown by some qualitative observations of the hydrolysis of quaternary hydrazones in aqueous acid and base. The rates were compared by recording the time required for turbidity (insoluble ketone) to appear. Hydrolysis was strongly accelerated by alkali, but not appreciably affected by acid.



$$C_6H_5-\underset{\underset{\text{II}}{CH_3}}{C}{=}N-\overset{+}{N}(CH_3)_3\ I^- \xrightarrow{\text{NAOEt}} C_6H_5-\underset{CH_2}{C{=}N} + N(CH_3)_3$$

$$C_6H_5-\underset{CH_2}{C{=}N} \xrightarrow{H_2O} C_6H_5COCH_2NH_2$$

This and the several additional examples reported in the Experimental Section are believed to be the first hydrazone rearrangements which are strictly analogous to oxime rearrangements. A previously reported example, the conversion of benzophenone hydrazone to benzanilide by treatment with nitrous acid,[7] is essentially an analog of the Schmidt reaction, in common with which it presumably possesses the azide intermediate III.



$$(C_6H_5)C{=}O + HN_3 \xrightarrow[H_2SO_4]{-H_2O} \underset{\text{III}}{(C_6H_5)_2C{=}N-\overset{+}{N}_2} \xleftarrow[H_2SO_4]{-H_2O} (C_6H_5)_2C{=}N-NH_2 + HNO_2$$

The spectrographic characteristics of the dimethylhydrazones, their methiodides, and the parent ketones are summarized in Table I. Infrared absorptions assignable to C=N vibration fell in the range 1588–1645 cm.$^{-1}$ The electronic spectra of the benzophenone series are illustrated in Fig. 1 as representative of the class, together with benzophenone *O*-methyloxime for comparison.

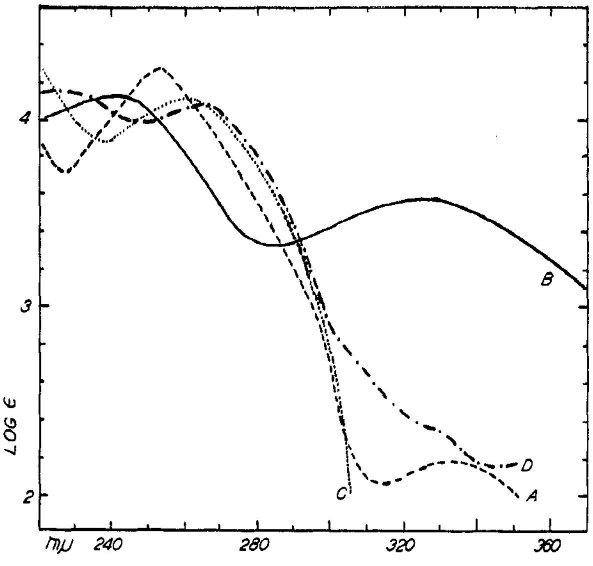


Fig. 1. Ultraviolet Absorption Spectra of Benzophenone (A, ----), its Dimethylhydrazone (B, ——), its N,N,N-Trimethyl Hydrazonium Iodide (C, ...), and its O-Methyl Oxime (D, —·—).

The conversion of the aryl ketones to their dimethylhydrazones resulted in a shift (9 to 33 mμ) to shorter wave lengths of the band attributed to absorption by the conjugated system C=N plus aryl. This was to be expected in view of the gen-

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[4] W. Theilacker and O. R. Leichtle, *Ann.*, **572**, 121 (1951).

[5] A. W. Chapman and F. A. Fidler, *J. Chem. Soc.*, 448 (1936).

[6] P. W. Neber, A. Burgard, and W. Thier, *Ann.*, **526**, 277 (1936).

[7] D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Am. Chem. Soc.*, **75**, 5905 (1953).

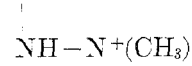
erally greater difficulty of developing a negative charge on nitrogen compared to oxygen, implying a corresponding destabilization of the excited state most closely resembling a structure with charge separation of the type . By contrast, the addition of a third methyl group to the terminal nitrogen, forming a quaternary ammonium ion there, resulted in a pronounced shift (12 to 39 mμ) of the absorption of the conjugated system to longer wavelengths. This corresponds to the charge separation of the type just mentioned being stabilized by the positive charge centered on the terminal nitrogen, adjacent to the generated negative charge. The large bathochromic shifts occurring on quaternization of dibenzyl ketone dimethylhydrazone, 72 and 50 mμ, are anomalous, since the chromophore systems are insulated by methylene groups from conjugation with the benzene rings. This may indicate an enamine structure,  $C_6H_5{-}CH{=}C(NH{-}N^+(CH_3)_3){-}CH_2{-}C_6H_5$. Neither acetophenone nor pinacolone showed this effect.

TABLE I

Characteristic Absorption Bands of Some Dimethylhydrazones and Their Methiodides

Compound	Ultraviolet λ_{max}, mμ	$\epsilon \times 10^{-4}$	Infrared[a] ν, cm.$^{-1}$
Benzophenone	252	1.82	
	335	.016	
Benzophenone D.M.H.[b]	242	1.31	1588
	330	.038	
Benzophenone T.M.H.[c]	262	1.32	1618
Dianisyl ketone	220	1.78	
	293	2.34	
Dianisyl ketone D.M.H.	262	1.99	1639
	334	.41	
Dianisyl ketone T.M.H.	224	3.16	1613
	299	1.99	
Acetophenone[d]	240	1.58	
	280	.12	
Acetophenone D.M.H.	237	.10	1640
	315	.022	
Acetophenone T.M.H.	248	1.07	1640
Dibenzyl ketone D.M.H.	220	1.3	1640
	295	.063	
Dibenzyl ketone T.M.H.	292	1.00	
	345[e]	.13	
Pinacolone D.M.H.	270	.085	1630
Pinacolone T.M.H.	<220	>1.35	
Diisobutyl ketone D.M.H.	280	.063	1640

[a] Additional data: cyclohexanone D.M.H., 1640; benzyl methyl ketone D.M.H., 1645. [b] Dimethylhydrazone. [c] Trimethylhydrazonium iodide. [d] D. J. Cram and J. D. Knight, *J. Am. Chem. Soc.*, **74,** 5840 (1952). [e] Shoulder.

EXPERIMENTAL

Acetophenone dimethylhydrazone. A mixture of 30 g. (0.25 mole) of acetophenone and 23 ml. (0.33 mole) of anhydrous dimethylhydrazine was heated on a steam bath under reflux, with protection from moisture, for 19 hr. The two layers which resulted were separated, and the aqueous layer was extracted with 100 ml. of ether. The combined organic layers were dried over potassium carbonate and distilled through a 13 × 180 mm., vacuum-jacketed, helix-packed column, to give 29.8 g. (13.6%) of acetophenone dimethylhydrazone, b.p. 97–102°/10 mm. The main portion (25.4 g.), which distilled at 100.5–102.0°/10 mm., was redistilled at 0.07 mm., b.p. 41.3°, n_D^{25} 1.5455, d_4^{25} 0.9689.

Anal. Calcd. for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70. Found: C, 73.65; H, 8.43.

A weighed sample was dissolved in excess 0.1*N* hydrochloric acid and back-titrated with 0.1*N* sodium hydroxide. The neutralization equivalent found was 162 (calcd. 162), and the *p*H at the inflection point was 4.2, from which value plus the known concentration can be estimated a value of 1.6×10^{-7} for K_b. The solution remained clear, indicating that hydrolysis to acetophenone was inappreciable.

Phenylacetone dimethylhydrazone. Reaction was vigorous and exothermic when 25 ml. of dimethylhydrazine and 33.6 g. of phenylacetone were mixed, and droplets of water began to separate. Refluxing was continued on a steam bath for 4 hr., and the layers were then separated with the help of ether. The organic layer was dried and distilled as before, to yield 33.5 g. (76%) of pale yellow phenylacetone dimethylhydrazone, b.p. 101.5–102.0°/10 mm. An analytical sample boiled at 57.1°/0.6 mm. Evaporative distillation at 40°/0.6 mm. did not remove the color; n_D^{25} 1.5156, d_4^{25} 0.9395.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15. Found: C, 74.87; H, 9.01.

The remaining dimethylhydrazones were prepared in essentially the same manner. The aromatic ketones reacted quite slowly, and required sealed tubes for efficient preparation. The branched aliphatic ketones reacted sluggishly in accordance with the degree of steric hindrance near the carbonyl group, and the unbranched aliphatic ketones reacted vigorously. The results are summarized in Table II.

Quaternary hydrazones. These derivatives were made by treating the dimethylhydrazines with methyl iodide in absolute ethanol or excess methyl iodide as solvent, for up to 4 hr. at reflux, or up to 4 days at room temperature. The products crystallized directly from the cold reaction mixtures; further crops were usually obtained by dilution with ether. Analysis was accomplished by the Volhard iodide determination. The results are given in Table III.

Hydrolysis of quaternary hydrazones: acetophenone. A solution of acetophenone trimethylhydrazonium iodide in 5 ml. of water and 20 ml. of concd. hydriodic acid was refluxed for 5 hr. The cooled mixture was extracted with 80 ml. of ether in four portions. The extracts were washed free of iodine with sodium bisulfite solution, 100 ml. of ethanol was added, the ether was removed by distillation, and the residual solution was treated with 2,4-dinitrophenylhydrazine in concd. hydrochloric acid. There was obtained 2.42 g. (76.5%) of acetophenone 2,4-dinitrophenylhydrazone, m.p. 239–242°.

The aqueous solution from the hydrolysis was evaporated to near dryness on a steam bath, and then completely dried by addition of absolute ethanol and distillation to dryness under aspirator vacuum. The residue of *N,N,N*-trimethylhydrazinium iodide weighed 1.85 g. (85%), m.p. 258°, after washing with absolute ethanol.

Benzophenone. To a solution of 4.16 g. of benzophenone trimethylhydrazonium iodide in 30 ml. of 95% ethanol was added 0.5 g. of sodium. After solution was complete, refluxing was continued for 2 hr. On chilling, 1.96 g. (85%) of *N,N,N*-trimethylhydrazinium iodide crystallized, m.p. 258° alone and when mixed with authentic material, depressed when mixed with trimethylammonium iodide.

Anal. Calcd. for $C_3H_{11}N_2I$: I, 67.9; Found; I, 68.3.

The filtered solution was concentrated to 15 ml. and 30 ml. of ether was added to precipitate sodium iodide which was filtered off. The ether was removed by distillation, 115 ml. of ethanol was added, and then 2.3 g. of 2,4-dinitrophenylhydrazine in 5 ml. of concd. hydrochloric acid. There was ob-

TABLE II

PREPARATION AND PROPERTIES OF DIMETHYLHYDRAZONES

Dimethylhydrazone of	B.P., °C.	Mm.	Yield, %	n_D^{25}	d_4^{25}	Mol. Ref.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
$(C_6H_5CH_2)_2C{=}O$	114 183.5–185.5	0.3 13	77	1.5544[a]	—		80.92	7.99	80.77	7.78
$(C_6H_5)_2C{=}O$	101	0.3	78[b]	1.6057	1.0424	74.18	80.32	7.19	80.25	6.91
t-$BuCH_3C{=}O$	130	740	76	1.4261	0.7930	45.97	67.56	12.75	67.47	12.34
$(i$-$Bu)_2C{=}O$	70–71	9.5	62	1.4347	0.8012	60.00	71.68	13.12	71.50	12.85
	59–60	11.5	66	1.4728	0.8962	43.86[d]	68.53	11.50	68.50	11.36
$(p$-$CH_3OC_6H_4)_2C{=}O$	—[c]	—	34	—	—		71.80	7.10	71.70	6.80
$C_6H_5(CH_3)C{=}O$	41.3 100.5–102	0.07 10	74	1.5455	0.9689	50.91	74.03	8.70	73.65	8.43
$C_6H_5CH_2(CH_3)C{=}O$	57.1 101.5–102	0.6 10	76	1.5156	0.9395	56.63	74.95	9.15	74.87	9.01

[a] At 31°. [b] Weighed as the hydrochloride. [c] M.p. 72–77°. [d] Lit.[2] 43.70.

TABLE III

N,N,N-Trimethylhydrazonium Iodides

Quaternary Hydrazone of	M.P., °C.	Yield, %	Analysis % I, Calcd.	% I, Found
Acetophenone	145–148	88	41.7	41.5
Dibenzyl ketone	147–147.1	44	32.2	32.1
Benzophenone	171–172.5	73	34.65	34.8
Pinacolone	168–169	81	44.7	44.3
Diisobutyl ketone	60–80	52	38.8	38.3
Dianisyl ketone	177–180	88	29.8	30.8
2,4-Dinitrophenylacetone	157–160	61[a]	31.1	31.2

[a] Based on the ketone; the dimethylhydrazone was not isolated.

tained 4.16 g. (100%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 233–237°; recrystallization raised this to 236–239° (reported 239°).

Rearrangement reactions: (A) acetophenone. A solution prepared by dissolving 0.25 g. of sodium in 15 ml. of absolute ethanol dried by distillation from magnesium ethoxide was added to a mixture of 3.05 g. of acetophenone trimethylhydrazonium iodide and 25 ml. of anhydrous ethanol, oven-dried glassware being used throughout. The mixture was refluxed for 22 hr. On cooling, 0.33 g. of trimethylhydrazinium iodide separated, m.p. 239° dec.

Anal. Calcd. for $C_3H_{11}N_2I$: I, 67.9. Found: I, 68.0.

Water was added to the filtered solution and part of the alcohol was removed on a steam bath. The oil which separated was taken up in ether, dried over potassium carbonate, and treated with dry hydrogen chloride. There was obtained 0.60 g. (35%) of crude phenacylamine hydrochloride, m.p. 179–186° dec.; after two recrystallizations the m.p. was 190–194° dec., undepressed when mixed with authentic phenacylamine hydrochloride. In another run, which was handled in a closed system to effect a more rigid exclusion of water, a yield of 67% was obtained. The benzoyl derivative was prepared by the addition of sodium hydroxide solution to a chilled mixture of a water solution of the amine hydrochloride and benzoyl chloride. The product melted at 123.5–126.5° after two recrystallizations from ethanol, and gave no depression when mixed with authentic *N*-benzoylphenacylamine.

B. Phenylacetone. The quaternary hydrazone was prepared *in situ* by the addition of 2 ml. of methyl iodide to a solution of 4.74 g. of phenylacetone dimethylhydrazone in 15 ml. of anhydrous ethanol. After 24 hr. at room temperature and 2.5 hr. at reflux temperature, the solution was made alkaline by the addition of 0.62 g. of sodium, and heating was continued for 1.5 hr. Trimethylamine was noticeable during this period.

Sodium iodide was filtered from the cooled mixture, and 50 ml. of 3% sodium carbonate solution was added, precipitating the presumed dihydropyrazine as a red oil. Fifty ml. of water was added, the mixture was concentrated slightly to remove alcohol, and the oil was taken up with 100 ml. of ether in three portions. Passage of hydrogen chloride through the ethereal extracts precipitated a dark red oil which slowly changed to yellow granules. The filtrate from these yielded a further quantity of product by evaporation to dryness with 15 ml. of 5% hydrochloric acid and trituration with 13 ml. of 1:3 ethanol-ether mixture. The total recovery of crude 1-amino-1-phenylacetone hydrochloride was 1.03 g. (22%), m.p. 184–188° dec.

In another experiment on a smaller scale the reaction mixture was allowed to stand at room temperature for 4 hr. after the addition of sodium, and was then filtered from precipitated salts and taken to dryness on a steam bath under aspirator vacuum. The residue was taken up in ether, filtered from residual salts, and treated with 10 ml. of concd. hydrochloric acid and 10 ml. of ethanol. The mixture was again taken to dryness, and the residue triturated with an ethanol-ether mixture, to yield 0.60 g. (20%) of grayish granules, m.p. 187–192° dec. Recrystallization from absolute ethanol gave 0.43 g. of material melting at 201–202° dec. (reported for 1-phenyl-1-aminoacetone hydrochloride, 208°). A portion of this product treated with benzoyl chloride under Schotten-Baumann conditions gave fine, colorless needles (from petroleum ether) of 1-phenyl-1-benzamidoacetone, m.p. 105–107°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.88; H, 5.97. Found: C, 76.09; H, 5.74.

C. Dibenzyl ketone. To a solution prepared from 40 ml. of anhydrous ethanol and a 0.17 g. piece of freshly cut sodium was added 2.84 g. of dibenzyl ketone trimethylhydrazonium iodide. After 18 hr. of refluxing, the cooled mixture was filtered from a little precipitated solid, placed in an ice bath, and diluted with 50 ml. of water. A red oil separated at once, but most of the alcohol was evaporated before the oil was taken up in 100 ml. of ether. After treatment with decolorizing charcoal and drying over potassium carbonate, the ethereal solution was concentrated to 50 ml. and treated with hydrogen chloride. The originally yellow solution turned through red to black and then lightened to orange-red as the hydrogen chloride was passed in. When only a small precipitate appeared, the mixture was concentrated to about 20 ml. and refrigerated overnight. A pale yellow powder, 0.42 g., m.p. 219–221°, was filtered off. A further 0.13 g. was obtained by evaporation of the filtrate with hydrochloric acid and triturating the residue with 1:3 methanol-ether; total yield of crude α-aminodibenzyl ketone hydrochloride, 29%. A sample for analysis was prepared by recrystallization from ethanol.

Anal. Calcd. for $C_{15}H_{16}ClNO$: C, 68.83; H, 6.16. Found: C, 68.95; H, 5.96.

In another experiment, the amino ketone was precipitated from the reaction mixture as a dark red oil by the addition of *p*-toluenesulfonic acid; it became pale yellow on standing in the mother liquor overnight, but did not crystallize. The oil was dissolved in water, washed with ether, and crystallized by evaporation to dryness repeatedly with absolute ethanol, followed by chilling to −17° of its solution in 3 ml. of absolute ethanol. There was obtained 0.44 g. (11%) of the toluenesulfonate, m.p. 182–190° dec. (reported 198°). Half of this was alkalized with ammonia, and the oil which separated was taken up in ether, with ample exposure to air. Crystallization could not be effected from ether or glacial acetic acid, but eventually the use of ethanol gave 0.08 g. of 2,5-dibenzyl-3,6-dimethylpyrazine, m.p. 135–151°; recrystallization from ethanol raised this to 149–151° (reported, 152°).

D. Pinacolone. Similar experiments with pinacolone trimethylhydrazonium iodide gave no detectable odor of trimethylamine, and no hydrochloride was obtained by the methods used with the foregoing compounds. In one such experiment the reaction mixture was concentrated by distillation and heated at 165–175° for 1 hr., but still no aminopinacolone could be found.

E. Benzophenone. A solution of 3.66 g. (0.01 mole) of benzophenone dimethylhydrazone methiodide and 0.734 g. (0.0105 mole) of sodium ethoxide in 40 ml. of magnesium-dried ethanol was refluxed for 3.5 hr. No trimethylamine could be detected at the top of the condenser. Most of the alcohol was then distilled and the residual mixture of yellow solid and red oil was held at 130° for 15 min. The resulting material was completely soluble in absolute ethanol, but water dissolved the solid and left a yellow oil. Treatment of the oil with hydroxylamine in alcoholic sodium hydroxide gave 1.22 g. (63%) of benzophenone oxime, m.p. 141.5–144° after recrystallization from methanol. No other organic product could be isolated, and it was concluded that rearrangement did not take place.

F. p,p'-Dimethoxybenzophenone. Under conditions similar to the foregoing, with refluxing for 14.5 hr., unchanged p,p'-dimethoxybenzophenone dimethylhydrazone methiodide was recovered in 85% yield.

Absorption spectra. Infrared absorption spectra were determined in carbon tetrachloride solution for the ketones and dimethylhydrazones, on a Baird Associates single-beam instrument with sodium chloride prism. The spectra of the quaternary hydrazones were determined in Nujol mulls, on a Perkin-Elmer single-beam instrument.

The ultraviolet spectra were determined over the range 220–370 mμ in approximately $10^{-4}M$ solution in ethanol with a Beckman model DU instrument.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

Mechanism of the Willgerodt Reaction. Studies with 1-Tetralones[1]

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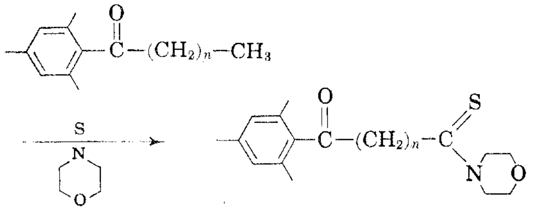
The reaction of 6-methoxy-1-tetralone with sulfur and morpholine yielded 6-methoxy-2-morpholinonaphthalene, showing attack occurred on the carbon atom adjacent to the carbonyl group. The role of a 2-morpholino-1-tetralone and a 1,2-dihydronaphthalene in this reaction was studied and it was shown that neither compound was an intermediate. The mechanism of the Willgerodt reaction is discussed.

The Willgerodt reaction with acylmesitylenes recently was investigated in this laboratory[1] and it was found that although the terminal methyl group was oxidized to a thioamide, the original carbonyl group of the acylmesitylene was retained. Such results clearly showed that contrary to previously postulated mechanisms,[3,4] neither addition to the carbonyl group nor reduction of the carbonyl group was an essential step in the Willgerodt reaction. Accordingly, the following modification of the mechanistic scheme of King and McMillan[3] was proposed: first, dehydrogenation to an α,β-unsaturated ketone; second, migration of the unsaturated linkage down the chain; third, an irreversible oxidation of the terminal carbon atom; and fourth, reduction of the carbonyl anytime after initial attack on the α-carbon atom. The first step possibly could involve attack on an α-carbon by sulfur followed by loss of hydrogen sulfide or displacement of the α-sulfur moiety by an amine to form an α-aminoketone which, in turn, could lose a molecule of amine to yield the α,β-unsaturated intermediate. The second step, *i.e.* migration of the unsaturated linkage, could proceed as suggested by King and McMillan[3] by reversible additions and eliminations of an amine or hydrogen sulfide to the olefinic linkage.



In order to gain evidence for some of these postulated intermediates it is necessary to study a system in which the final irreversible oxidation stage is prohibited. One such study has been reported by

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(1) For the previous paper in this series, see W. G. Dauben and J. B. Rogan, *J. Am. Chem. Soc.*, 78, 4135 (1956).

(2) Recipient of the U. S. Rubber Co. Fellowship in Chemistry, 1954–55.

(3) J. A. King and F. H. McMillan, *J. Am. Chem. Soc.*, 68, 632 (1946).

(4) M. Carmack and D. F. DeTar, *J. Am. Chem. Soc.*, 68, 2029 (1946).