Table II

Molar proportion of		% excess of chlorosulfonic acid	% yield of disulfonamide
Diphenoxypropane	Chlorosulfonic acid		
1	4	0	26
1	5	25	85
1	6	50	83
1	8.5	112	64

The disulfonamide, after recrystallization from an ethanol-methyl ethyl ketone mixture, was in the form of feather-like clusters, m. p. 194.5–195°[7] (see Table I for analysis). The structure of the material prepared in these Laboratories has been unequivocally proved, as will be shown in the following paragraph.

N,N,N′,N′-Tetramethyl-α,γ-diphenoxypropane-4,4′-disulfonamide (IV). A.—A portion of the same chloroform solution of α,γ-diphenoxypropane-4,4′-disulfonyl chloride, of which part had been used to prepare the amide III, m. p. 194.5–195°, was treated with an excess of aqueous dimethylamine. The resultant solid, after two recrystallizations from ethanol, was in the form of flaky crystals, m. p. 191° (see Table I for analysis).

B.—A mixture of 4-hydroxybenzenesulfondimethylamide[1] (620 mg., 3.1 millimoles), potassium hydroxide (175 mg., 3.1 millimoles), and trimethylene bromide (300 mg., 1.5 millimoles) in ethanol (10 cc.) was refluxed one hour. The mixture was poured into water and the white solid formed was recrystallized once from ethanol then once from methanol; m. p. 187–189°. When this substance (m. p. 187–189°) was mixed with a sample of the same material (m. p. 191°) prepared by procedure A, the mixture melted at 188–190°.

N,N′-Diethyl-α,γ-diphenoxypropane-4,4′-disulfonamide (V).—α,γ-Diphenoxypropane-4,4′-disulfonyl chloride (42.5 g., 0.10 mole, crude, m. p. 116–117°) dissolved in chloroform (200 cc.) was stirred at room temperature for forty five minutes with aqueous ethylamine (100 g. of 33% solution, 0.73 mole), the chloroform was separated and the

(7) A compound of m. p. 245–255° prepared in 44% yield from α,γ-diphenoxypropane with chlorosulfonic acid, and giving satisfactory analyses, was reported by Huntress and Carten.⁴ In the light of results reported in the present paper, however, their product could not have been α,γ-diphenoxypropane-4,4′-disulfonamide.

solvent was removed to leave the crude product (33.0 g.), m. p. 138–142°. After recrystallization from ethanol it weighed 30.7 g. (69% yield) and melted at 143.5–144° (see Table I for analysis).

N,N′-Diacetyl-α,γ-diphenoxypropane-4,4′-disulfonamide (VI).—A mixture of α,γ-diphenoxypropane-4,4′-disulfonamide (31.5 g., 0.0815 mole) and acetic anhydride (250 cc.) was refluxed one hour then poured onto ice and allowed to stand overnight. The solid product (m. p. 163–168°) was recrystallized from aqueous acetic acid to give the pure diacetyl derivative (25.6 g., 67% yield), m. p. 169–170° (see Table I for analysis).

The material crystallizes as a monohydrate and if the sample is dried in a vacuum at not over 80° it analyzes for a monohydrate.

Anal. Calcd. for $C_{19}H_{22}N_2O_8S_2 \cdot H_2O$: C, 46.71; H, 4.92; N, 5.73. Found: C, 46.73; H, 4.72; N, 5.92.

The diacetyl derivative VI (25.0 g., 0.0512 mole of monohydrate) was dissolved in 106 cc. of 0.962 N sodium hydroxide (the theoretical amount), the solution was evaporated to a thick paste and the residue was triturated with ethanol to give the white solid disodium salt VII (see Table I for analysis).

Summary

1. α,γ-Diphenoxypropane has been converted by chlorosulfonic acid followed by ammonia into the 4,4′-disulfonamide.

2. The orientation of the two chlorosulfonyl groups entering the molecule has been proved by showing that an amide prepared from the disulfonyl chloride is identical with that synthesized directly from the corresponding 4-hydroxybenzenesulfonamide and trimethylene bromide.

3. The following four other N-substituted disulfonamides were prepared: dimethyl, ethyl acetyl, and sodio-acetyl.

4. None of these compounds have trypanocidal activity.

NOTES

Mechanism of the Reaction between Hindered Allyl Esters and Grignard Reagents

By Richard T. Arnold and R. Winston Liggett[1]

In two previous publications from this Laboratory[2,3] it was shown that allylic esters of hindered carboxylic acids react with Grignard reagents to give hydrocarbons and halomagnesium salts according to the following equation.
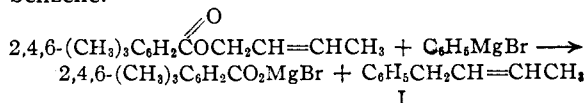
$$R-C{\overset{O}{\underset{OCH_2CH=CH_2}{\big\langle}}} + R'MgX \longrightarrow$$

$$R-C{\overset{O}{\underset{OMgX}{\big\langle}}} + R'CH_2CH=CH_2$$
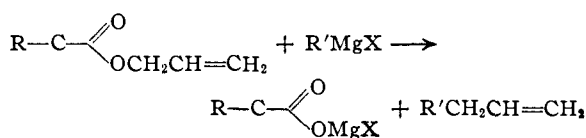
(1) Dupont Post Doctorate Fellow 1941–1942.
(2) Arnold, Bank and Liggett, This Journal, **63**, 3444 (1941).
(3) Arnold and Liggett, *ibid.*, **64**, 2875 (1942).

An experimental result obtained over a year ago has forced us to make some drastic alterations in the mechanism proposed earlier.² It has been found that the olefin produced when phenylmagnesium bromide is allowed to react with n-crotyl mesitoate is pure n-crotylbenzene (I) and apparently contains none of the isomeric isocrotylbenzene.

$$2,4,6\text{-}(CH_3)_3C_6H_2\overset{O}{\overset{\|}{C}}OCH_2CH=CHCH_3 + C_6H_5MgBr \longrightarrow$$
$$2,4,6\text{-}(CH_3)_3C_6H_2CO_2MgBr + C_6H_5CH_2CH=CHCH_3$$
$$\text{I}$$

This seems of especial interest since it is well known that either of the pure isomeric crotyl halides gives a mixture of isomeric hydrocarbons when treated with the Grignard reagent.

We believe that the new mechanism outlined

below offers an accurate description of the reaction which is under investigation in these Laboratories.

$$R''—C\diagup^{O}_{\diagdown OCH_2CH=CHR'} + RMgX \longrightarrow$$

$$\left[\begin{array}{c} X \\ | \oplus \\ R''—C\diagup^{O\cdots Mg}_{\diagdown O——CH_2CH=CHR'} \,\widehat{R}\ominus \end{array}\right] \longrightarrow$$

II

$$R''—C\diagup^{O—MgX}_{\diagdown O} + RCH_2CH=CHR'$$

By inspection of II it can be seen that group R (from RMgX) is one element of a quasi six-membered ring and because of this fact it is geometrically in a position such that it must attack only the α-carbon atom of the allylic system $\left(\begin{smallmatrix}\alpha & \beta & \gamma\\ —CH_2—CH=CH—R'\end{smallmatrix}\right)$ when the redistribution of electrons (as indicated by the arrows) is completed. We regard the breaking and formation of bonds in the decomposition of II as occurring simultaneously.

When conditions permit, a systematic investigation to prove or disprove this newly proposed mechanism will be undertaken.

Experimental

n-Crotyl Mesitoate.—This ester was prepared from pure *n*-crotyl alcohol, mesitoyl chloride and pyridine in cold chloroform solution as described earlier in other examples; yield 58%; b. p. 160–165° (17 mm.).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.3. Found: C, 76.8; H, 8.7.

The ester on ozonolysis gave acetaldehyde as the sole volatile aldehyde.

n-Crotylbenzene.—Cleavage of *n*-crotyl mesitoate with phenylmagnesium bromide as described earlier[2] for other examples gave a hydrocarbon; yield 75.5%; b. p. 81–83° (22 mm.). (Reported 81–82° (18 mm.).[4])

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 91.0; H, 9.15.

This hydrocarbon gave acetaldehyde as the only identifiable volatile aldehyde. Catalytic hydrogenation gave a non-olefinic hydrocarbon whose vapor pressure curve was identical with pure *n*-butylbenzene and quite different from that of *s*-butylbenzene.

(4) Auwers, Roth and Eisenlohr, *Ann.*, **383**, 108 (1911).

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1,2,5,6-Diacetone *d*-Mannitol and 1,2,5,6-Diacetone *l*-Mannitol

By Erich Baer

The chemical synthesis of pure enantiomorphs of optically active compounds of biological interest often involves the use of difficultly accessible intermediates. The recently described syntheses of the enantiomorphs of a number of unsymmetrically substituted glycerols have been laborious because of the commercial unavailability and the lack of an efficient synthesis of the 1,2,5,6-di-

acetone derivatives of *d*- and *l*-mannitol. The key position of these two compounds is illustrated by the fact that they have become essential intermediates in the synthesis of *d*(+)α-glycerophosphate,[1] *l*(−)α-glycerophosphate,[2] the normal aliphatic α-monoglycerides,[3,4] α,β-diglycerides,[5] triglycerides,[3] batyl alcohol,[6] chimyl alcohol,[6] and selachyl alcohol.[7] Since the number of applications can be expected to increase, the importance of finding an improved method of preparing these mannitol derivatives is obvious when one considers the labor involved in the older methods.

The first synthesis and description of 1,2,5,6-diacetone *d*-mannitol was given by E. Fischer and Rund in 1916.[8] They obtained the substance on acetonation of *d*-mannitol with acetone and hydrochloric acid, but in a yield of 2% only. By changing the solvent used for extracting the product from the reaction mixture Fischer and Baer in 1934[9] succeeded in raising the yield of this process to approximately 6%. An entirely different procedure was reported by von Vargha,[10] who conducted the acetonation with concd. sulfuric acid in the presence of boric acid. The resulting boric acid ester (4.5) of 1,2-acetone *d*-mannitol was freed from boric acid by alcoholysis and the second acetone introduced by acetonation with copper sulfate. The yield was still very low (14%); moreover, the outcome of the synthesis was unpredictable. With the chemicals then (1934) available in Basel (Switzerland) we succeeded only twice out of many trials in obtaining any yield of diacetone *d*-mannitol. It is possible that some reactant in the successful preparations contained a contaminant which acted as a catalyst for the condensation.

The successful application of zinc chloride as catalyst in other acetonation reactions [Fischer and Taube,[11] Fischer and Baer[12]] prompted a study of its use for the preparation of the diacetone mannitols. These studies resulted in 1939 in the development of a quite satisfactory method (Baer and Fischer[13a,13b]), the yields being raised to 56%, but owing to the labor involved in the removal of large amounts of zinc chloride and solvents the method as described then was still cumbersome and only applicable to small scale preparation. The consequent necessity of repeating the synthesis at fre-

(1) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **135**, 321 (1940).

(2) E. Baer and H. O. L. Fischer, *ibid.*, **128**, 491 (1939).

(3) E. Baer and H. O. L. Fischer, *ibid.*, **128**, 475 (1939).

(4) E. Baer and H. O. L. Fischer, communication in preparation for This Journal.

(5) J. C. Sowden and H. O. L. Fischer, This Journal, **63**, 3244 (1941).

(6) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **140**, 397 (1941).

(7) E. Baer, L. Rubin and H. O. L. Fischer, *ibid.*, **155**, 447 (1944).

(8) E. Fischer and C. Rund, *Ber.*, **49**, 91 (1916).

(9) H. O. L. Fischer and E. Baer, *Helv. Chim. Acta*, **17**, 622 (1934).

(10) L. von Vargha, *Ber.*, **66**, 1394 (1933).

(11) H. O. L. Fischer and C. Taube, *ibid.*, **60**, 485 (1927).

(12) H. O. L. Fischer and E. Baer, *ibid.*, **63**, 1749 (1930).

(13) (a) E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **128**, 463 (1939). (b) E. Baer and H. O. L. Fischer, This Journal, **61**, 761 (1939).

quent intervals in order to accumulate any quantity of this key intermediate compound proved very tedious.

During the past five years numerous small variations in the preparation have been given a trial. Several of the changes proved distinctly advantageous and their combination led to a procedure which is less time consuming, cheaper and which can be carried out easily on a larger scale. These improvements are the result of the following three major changes: (a) reduction of the amount of zinc chloride and acetone to one-third of the quantities originally used, (b) decrease of the reaction time from nineteen hours to approximately two hours and (c) the use of a better solvent (butyl ether instead of petroleum ether) for the isolation and crystallization of the diacetone d- or l-mannitol.

Experimental

Two hundred and seventy grams of zinc chloride sticks (Analytical reagent, Mallinckrodt) is dissolved in 1350 cc. of dry acetone. After the solution has cooled to room temperature and the insoluble matter has settled out, the slightly turbid supernatant liquid is decanted and added to 170 g. of finely powdered d- or l-mannitol which has been passed through a 200-mesh sieve. The mixture, protected against intrusion of moisture, is either shaken or vigorously stirred until most of the mannitol is dissolved. This operation usually requires about two hours at a room temperature of 19 to 20°. The solution is then filtered (recovering approximately 40 g. of unreacted mannitol) and the filtrate is immediately processed as follows.

In a 5-liter round-bottomed flask equipped with an efficient mechanical stirrer, reaching nearly to the bottom of the flask, are dissolved 340 g. of potassium carbonate (anhydrous) in 340 cc. of water; this solution is covered with 1350 cc. of dry ether.[14] The mixture is vigorously stirred while the filtered acetone-zinc chloride solution is poured in as rapidly as possible. The success of the preparation depends to a large extent upon the speed with which the reactants are brought together; thus the rate of addition and the efficiency of stirring are influential factors. The stirring is continued for a period of thirty to forty minutes, after which the ether-acetone solution is decanted and the zinc carbonate pellets are washed with several portions (totalling 300 to 400 cc.) of a 1:1 acetone-ether mixture. The combined solutions are dried by stirring with 340 g. of calcined potassium carbonate for thirty minutes. The solution is filtered and the carbonate is washed with several portions of a 1:1 acetone-ether mixture (totalling 300 cc. to 400 cc.). The combined filtrate and washings are evaporated under reduced pressure. The residue is finally dried in vacuo at 60 to 70° (waterbath) for two hours. The distilling flask is transferred to an oil-bath, 400 cc. of n-butyl ether added and the temperature of the bath raised to 135°. The hot solution is filtered rapidly, using a hot water funnel. Another 75-cc. portion of hot butyl ether is used to rinse the flask and filter. The filtrate, which solidifies immediately, is kept in ice for several hours. The precipitate is filtered with suction, washed with low boiling petroleum ether and dried in vacuo. The yield of 1,2,5,6-diacetone d- or l-mannitol is as high as 103 g. (55% of the theoretical amount based on the amount of mannitol in solution). The products melt from 117 to 119°. Recrystallization from water in which both acetone mannitols are very soluble occasions an appreciable loss but gives very pure products in the form of long, fine needles melting at 122°. Products, however, melting from 117 to 119° are pure enough for most purposes. Mixed melting points of 1,2,5,6-diacetone d- or l-mannitol thus prepared with corresponding enantio-

(14) The ether was freed from ethanol and water before use.

morphs prepared by other methods give no depression. Both compounds on oxidation with lead tetraacetate and subsequent hydrolysis yield quantitatively d- or l-glyceraldehyde, respectively.[15,16]

Anal. 1,2,5,6-Diacetone d-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.8; H, 8.5. 1,2,5,6-Diacetone l-mannitol $C_{12}H_{22}O_6$ (262.2). Calcd.: C, 54.9; H, 8.6. Found: C, 54.9; H, 8.5.

(15) E. Baer, J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, 61, 2607 (1939).

(16) E. Baer and H. O. L. Fischer, ibid., 61, 761 (1939).

On the Structure of Dimethyl Ether–Boron Trifluoride

BY S. H. BAUER, G. R. FINLAY AND A. W. LAUBENGAYER

Brown and Adams[1] called attention to a discrepancy in the data on the dissociation of dimethyl ether–boron trifluoride.[2] We reëxamined the data in question and agree that these are not self-consistent; it is likely that the dissociations we calculated for the lower temperature range are too low. Since our experimental method was such that no direct observation of the completeness of vaporization could be made, it is possible that in this lower temperature range the sample was not entirely in the vapor phase, as was assumed in our calculations. Consequently, the percentage dissociation we assumed in interpreting our electron diffraction photographs of dimethyl ether–boron trifluoride[3] was incorrect; instead of the negligible 10% dissociation for the saturated vapor at about 40° we should have taken a value close to 57% deduced from the combined data of Brown and Adams[4] and of Laubengayer and Finlay. We have therefore reconsidered our electron diffraction results assuming more extensive dissociation.

As will be recalled, our study began with a radial distribution computation. This approach is basic, since no assumption need be made regarding the structure or composition of the diffracting sample. The interatomic distances which must occur in the diffracting sample are indicated in Fig. 1a, curve R.D. Extensive experience has shown that the peaks which lie below 1 Å. or above 4 Å. cannot be trusted, due to the fact that the incomplete integrations introduce spurious oscillations in these regions; those peaks found between 1 and 2 Å., and between 3 and 4 Å. are within 3% of the interatomic distances obtained by more extensive analysis, while the range 2 to 3 Å. is most accurately represented (to 1–2%). Since in the unassociated molecules no interatomic distances above 2.36 Å. are present, the occurrence of peaks

(1) H. C. Brown and R. M. Adams, THIS JOURNAL, 65, 2253 (1943).

(2) A. W. Laubengayer and G. R. Finlay, ibid., 65, 887 (1943).

(3) S. H. Bauer, G. R. Finlay and A. W. Laubengayer, ibid., 65, 889 (1943).

(4) H. C. Brown and R. M. Adams, ibid., 64, 2559 (1942).
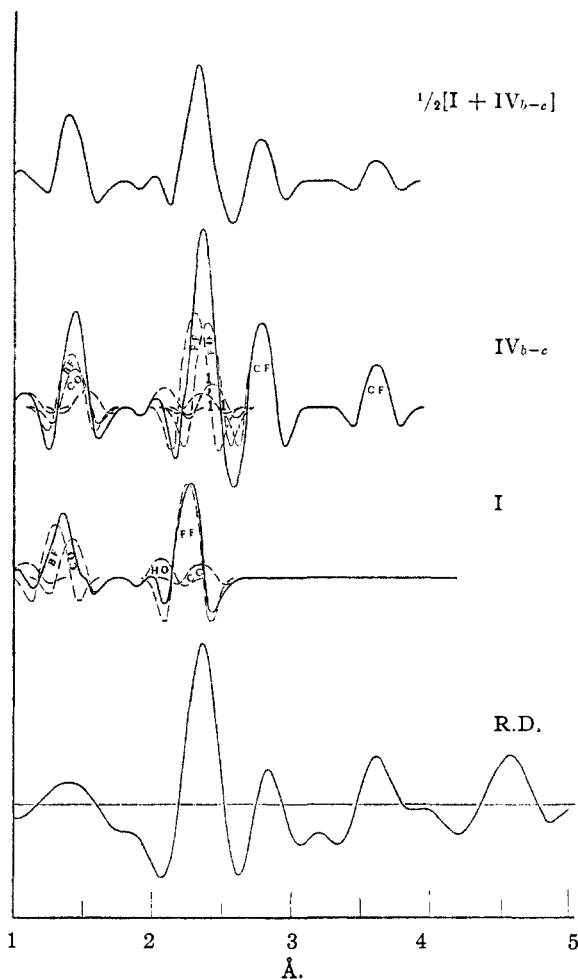
Fig. 1a.—Radial distribution curves for $(CH_3)_2O:BF_3$: R.D., curve obtained from the data; I, "synthetic" curve, complete dissociation; IV_{b-c}, completely associated (final model previously given); $\frac{1}{2}[I + IV_{b-c}]$, 50% dissociated (final model previously given).

at 2.84 Å. and 3.61 Å. clearly implies that an appreciable fraction of our sample was associated.

It is instructive to compare "synthetic" radial distribution curves for various models [I (unassociated); IV (0% dissociated–final model given previously[2]); and (I + IV)/2 (50% dissociated–final model)] with the one obtained from the photographs (Fig. 1a). Although it appears that a clear cut distinction cannot be made between 50 and 0% dissociation, the case of 100% dissociation and our previously designated models II and III may still be unquestionably eliminated. And, as has been pointed out in our original communication, the only question which remains is what configuration of IV, V or VI is in best agreement with the data. Further, the correct model must be essentially like IV, V or VI, since these give the critical peaks, due to the C–F interactions at the observed positions 2.8 Å. and 3.6 Å., and allow the F–F and F–O separations (which are the
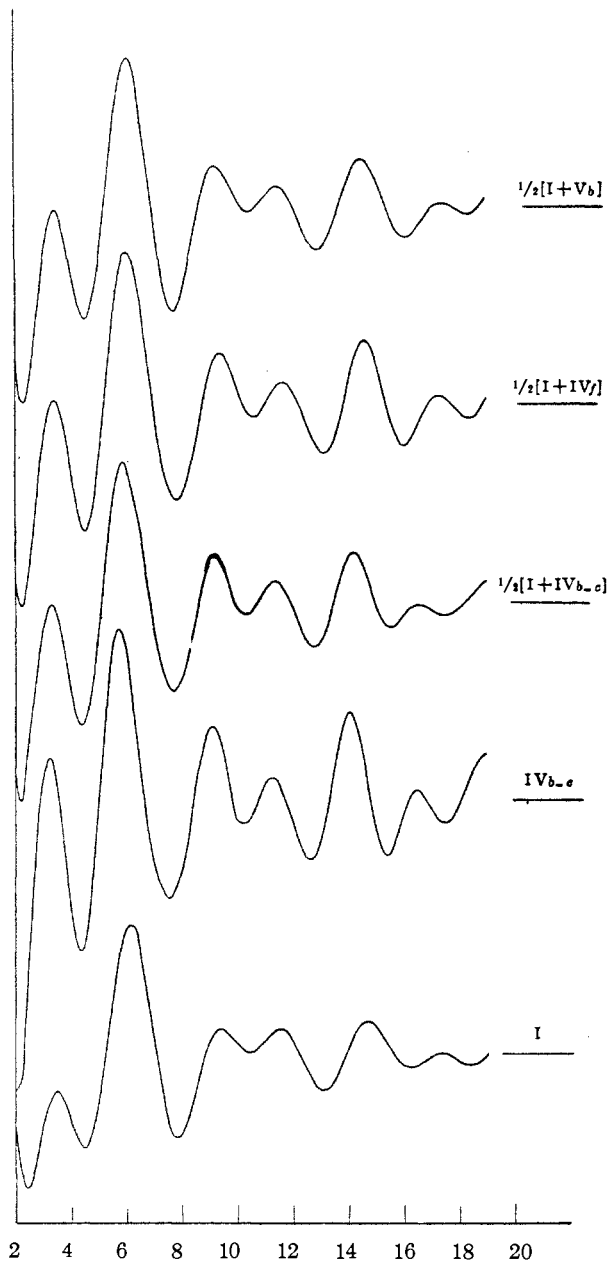
Fig. 2a.—Theoretical intensity curves for $(CH_3)_2O:BF_3$: I, completely dissociated; IV_{b-c}, completely associated (final model previously given); $\frac{1}{2}[I + IV_{b-c}]$; $\frac{1}{2}[I + IV_f]$; $\frac{1}{2}[I + V_b]$: models previously discussed, 50% dissociated.

principal components of the large peak at 2.36 Å.) to come close to one another. This is emphasized by the similarity of the curves in Fig. 1a, below 2.5 Å.; the F–F separations in the associated molecule have to be rather close to those in the unassociated BF_3, in spite of the formation of the new B–O bond, and consequent changes in ∠FBF's. This can only be accomplished by the simultaneous elongation of B–F to about 1.4 Å.

Our next consideration was to note how the curves in Fig. 3, reference 2, change, when one assumes an appreciable amount of dissociation. Theoretical intensity curves were therefore computed for models IVa, IVd, IVf, and IVb-c (final model previously given); also for V_a and V_b, assuming in each case that 50% of the sample was dissociated[5] (Fig. 2a). The resulting curves differ only slightly from those in which no dissociation was assumed (except for model IVa, which is no longer admissible); this is due to the fact that the amplitude of the intensity curve for the dissociated part of the sample, for $S > 8$, is only about half of the amplitude of the pattern of the associated molecules, while in the region $S < 8$ all the curves show the same qualitative features. The quantitative comparison is presented in Table Ia.

TABLE Ia

DIMETHYL ETHER–BORON TRIFLUORIDE

| | | | 0% dissociated | | $s_u(calcd.)/s_0(obs.)$ | 50% dissociated | | |
Max.	Min.	s_0	I_{Av}	IV_{b-c}	IV_{b-c}	IV_d	IV_f	V_b
1		3.22	7	1.003	1.025	1.037	1.056	1.068
	2	4.44	−5	0.982	0.991	1.009	1.013	1.018
2		5.76	10	.993	1.021	1.035	1.042	1.052
	3	7.61	−6	.992	1.012	1.024	1.026	1.022
3		8.88	4.2	1.028	1.036	1.048	1.056	1.038
	4	10.07	−3	1.016	1.029	1.039	1.051	1.036
4		11.32	3.5	.996	1.005	1.019	1.028	1.016
	5	12.68	−2.8	.999	1.009	1.023	1.035	1.020
5		14.08	2.2	1.000	1.010	1.026	1.037	1.031
	6	15.24	−1.5	1.012	1.021	1.039	1.051	1.058
6		16.43	1	1.004	1.010	1.036	1.049	1.059
Average				1.002	1.015	1.030	1.040	1.038
Mean deviation				0.0093	0.0100	0.0094	0.0115	0.0155
Interatomic distances deduced		B–F	1.41	1.43	1.432	1.446	1.443
		B–O	1.52	1.54	1.493	1.446	1.495
		C–O	1.44	1.46	1.483	1.498	1.495

On replotting the average deviations for models IV, the minimum (0.0093) is found to be shifted from $(B–F)/(B–O) = 0.925$ to $(B–F)/(B–O) = 0.955$ with the average value for $s_{calcd.}/s_{obs.} = 1.028$. Hence the structure which is in best qualitative and quantitative agreement with the data—assuming 50% dissociation—is:

Boron and oxygen valence angles tetrahedral
B–F = 1.43 ± 0.03 Å. (previously 1.41 ± 0.02 Å.)
B–O = 1.50 ± 0.06 Å. (previously 1.52 ± 0.06 Å.)
C–O = 1.45 ± 0.03 Å. (previously 1.44 ± 0.03 Å.)

The situation also remains unchanged with regard to models V and VI; quantitatively these are not as satisfactory as the above model, but they cannot be eliminated. Due to the introduction of another variable, the degree of dissociation of the diffracting sample, the limits of error imposed on the final B–F distance is of necessity increased.

The case of dimethyl ether–boron trifluoride turned out to be more favorable for a structure

(5) The exact per cent. dissociation in the sample doing the diffracting is not known. It probably was around 60%, as can be judged from the heights of the peaks at 2.84 Å. and 3.16 Å. of the R.D. curve. We assumed 50% dissociation rather than the somewhat larger value only because the computations are thus greatly simplified. We have shown below that the conclusions regarding the final structure are not sensitive to the fraction postulated.

determination than we had anticipated, due to the apparent insensitivity to the degree of dissociation of the complex. A similar electron diffraction attempt to determine the structure of the methyl cyanide–boron trichloride complex in the vapor phase clearly showed that the compound was completely dissociated at 95°, and this was substantiated by vapor density measurements.[6]

(6) A. W. Laubengayer and D. C. Sears, THIS JOURNAL, 67, 164 (1945).

The Production of a Poison for Nickel Catalysts in the Absorption of Oxygen by Fieser's Solution[1]

BY W. B. BURFORD, III, AND J. C. W. FRAZER

In the early stages of work on the poisoning of nickel hydrogenation catalysts by water vapor[2] an attempt was made to remove oxygen from the ethylene by means of alkaline hydrosulfite in the form of Fieser's solution number 2,[3] using an equivalent amount of potassium hydroxide in place of the sodium hydroxide specified. Highly erratic results followed which suggested that the solution might be introducing some impurity into the ethylene. This was confirmed by the disappearance of the effect when purification by means of a precatalyst tube was substituted for the Fieser's solution.

The odor of exhausted solutions strongly indicated a sulfur containing compound. Tests for sulfur dioxide and hydrogen sulfide were both negative, but a positive test for carbon disulfide was obtained by the procedure of Vogel.[4] This consists of passing the gases into alcoholic potassium hydroxide and precipitating any xanthate formed with copper sulfate as the dark yellow-green insoluble copper xanthate.

Tests were made by bubbling gas through the hydrosulfite solution at about 55 ml. per min. for one-half to one hour and passing the exit gases through alcoholic potassium hydroxide. The yellow-green color of the precipitate formed was observed readily against filter paper after filtration.

Using ethylene containing 2% oxygen a positive test was obtained in fifteen minutes. However, with 0.1% oxygen at least half an hour was required and it was necessary to heat the hydrosulfite. A faint positive test was obtained when air alone was passed through for fifteen minutes but none if pure nitrogen was used.

Various brands and purities of reagents produced no change in these observations.

It is concluded that the action of ethylene-oxygen mixtures or of air on Fieser's solution pro-

(1) Original manuscript received January 27, 1943.

(2) W. B. Burford, III, and J. C. W. Frazer, THIS JOURNAL, 67, 331 (1945).

(3) L. F. Fieser, ibid., 46, 2639 (1924).

(4) Vogel, Ann., 86, 369 (1853).

duces a detectable amount of a volatile material giving the xanthate test for carbon disulfide. Mere oxygen concentration does not seem to govern the amount produced, for the test with air was very faint. The results also strongly suggest that ethylene alone is without effect.

The poisoning effect of carbon disulfide on nickel catalysts is well known and may account for the erratic results obtained using Fieser's solution.

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Some Styrylpyridines and -Quinolines

BY H. GILMAN AND GEORGE KARMAS

Incidental to a study of anils, several substituted styrylpyridines and -quinolines have been prepared. Some of the nitrostyryl types were reduced to the corresponding aminostyryls, and these in turn were condensed with acetonylacetone to give the corresponding 2,5-dimethylpyrryl-styryl compounds. The following is an illustrative sequence of transformations:
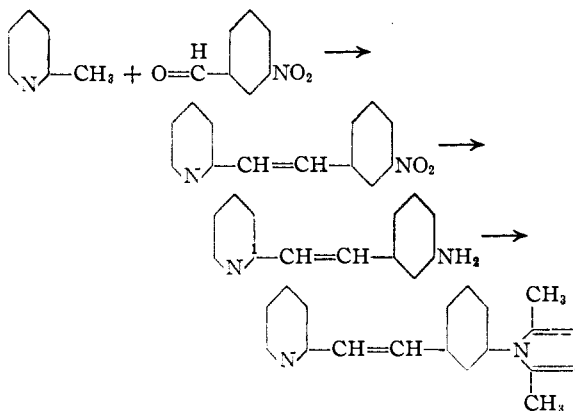
Experimental

The condensations of aldehydes with the picolines, quinaldine, and lepidine were effected by conventional procedures.[1,2] In a few comparative preparations it was observed that the method using acetic anhydride was better than the one in which anhydrous zinc chloride was used. The general results are given in Table I. Tests on the following compounds will also be reported later: α-(p-dimethylaminostyryl)-quinoline[3]; α-(m-aminostyryl)-quinoline[4]; α,α'-(di-m-nitrostyryl)-pyridine[5]; α- and γ-(m-nitrostyryl)-pyridine[2,5]; α-(m-nitrostyryl)-quinoline[6]; α-(p-nitrostyryl)-quinoline[7]; α-(m-2,5-dimethylpyrrylstyryl)-quinoline; α- and γ-(p-nitrostryl)-pyridine[2,5]; and α- and γ-(m-aminostyryl)-pyridines.[8]

The authors are grateful to Parke, Davis and Company for arranging the tests.

(1) Kaplan and Lindwall, THIS JOURNAL, 65, 927 (1943).

(2) Shaw and Wagstaff, J. Chem. Soc., 77 (1933).

(3) Noelting and Witte, Ber., 39, 2750 (1906). Our m. p. for this compound was 181–182°, and they reported 177°.

(4) Wartanian, Ber., 23, 3648 (1890). Our m. p. for this compound was 160–161°, and he reported 158–159°.

(5) Wagstaff, J. Chem. Soc., 277 (1934).

(6) Taylor and Woodhouse, ibid., 2971 (1926).

(7) Bulach, Ber., 20, 2047 (1887).

(8) See footnotes f and g in Table I.

TABLE I
STYRYL DERIVATIVES

Product	M. p. (cor.), °C.	Anal., % N Calcd.	Found
α,γ-(C$_5$H$_3$N)(CH=CHC$_6$H$_4$NO$_2$-m)$_2$[a]	242–243	10.80	11.02
γ-(C$_5$H$_4$N)CH=CHC$_6$H$_4$N(CH$_3$)$_2$-p[b]	240–241	12.50	12.37
γ-(C$_9$H$_6$N)CH=CHC$_6$H$_4$N(CH$_3$)$_2$-p[c]	141–142	10.23	10.36
γ-(C$_5$H$_4$N)CH=CHC$_4$H$_2$O-α (picrate)[d]	212–214	14.00	14.25
α-(C$_5$H$_4$N)CH=CHC$_6$H$_4$CF$_3$-m[e]	104–105	4.68	4.18
α-(C$_5$H$_4$N)CH=CHC$_6$H$_4$NH$_2$-m[f]	103–104	14.30	14.32
γ-(C$_5$H$_4$N)CH=CHC$_6$H$_4$NH$_2$-m[g]	189–190	14.30	14.45
α-(C$_5$H$_4$N)CH=CHC$_6$H$_4$NC$_6$H$_8$-m[h]	87–88	10.20	10.40
α-(C$_9$H$_6$N)CH=CHC$_6$H$_4$NC$_6$H$_8$-m[i]	132–133	8.63	8.70

[a] This condensation product of α,γ-lutidine and m-nitrobenzaldehyde was crystallized from tetrachloroethane. The yield was 34%. [b] Crystallization of the condensation product from p-dimethylaminobenzaldehyde was from methanol. [c] Crystallization was from petroleum ether (b. p. 80–110°). [d] The condensation product with furfural distilled at about 200° (18 mm.), and because of its instability in air was converted to the picrate which was crystallized from ethanol. [e] This compound was synthesized in 65% yield by condensation with m-trifluoromethylbenzaldehyde (prepared by F. Yeoman), and was crystallized from dilute ethanol. [f] The nitrostyrenes were reduced to the corresponding amines by refluxing an ethanol solution with a saturated aqueous solution of sodium sulfide. The hemi-hydrate of this m-aminostyryl derivative of α-picoline was reported to melt at 85° [Schuftan, Ber., 23, 2717 (1890)]. Our product, obtained in 49% yield, was crystallized from dilute ethanol. [g] No m. p. was given for this compound. See Deutsche Hydrierwerke Akt.-Ges., French Patent 775,101 (June 27, 1934) [Chem. Zentr., 106, I, 3853 (1935)]. Our product, obtained in 47% yield, was crystallized from ethanol. [h] The m-2,5-dimethylpyrrylstyryl compound, obtained by condensation of the m-aminostyryl product with acetonylacetone, distilled as a viscous light yellow oil at 180–190° (0.001 mm.). This solidified after a short time, and crystallization from dilute methanol gave small, colorless flakes. [i] The reduction of α-(m-nitrostyryl)-quinoline by sodium sulfide gave the corresponding amine in a 57% yield and melting at 160–161°. The m. p. reported by Wartanian, Ber., 23, 3648 (1890), is 158–159°. In addition to the amine we isolated a small quantity of an orange colored compound which was insoluble in hot ethanol, but crystallized from dioxane as fine, orange needles melting at 226–227°. This may be the azo compound, C$_9$H$_6$NCH=CHC$_6$H$_4$N=NC$_6$H$_4$CH=CHC$_9$H$_6$N. Anal. Calcd. for C$_{34}$H$_{24}$N$_4$: N, 11.46. Found: N, 11.21. The m-(3,5-dimethylpyrrylstyryl) product, obtained in 72% yield by condensation of the amine with acetonylacetone, distilled at 200–210° (0.001 mm.). Crystallization from ethanol gave fine, buff platelets.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA   RECEIVED OCTOBER 21, 1944

Fluorescence Chromatography of the Methyl Glucoses[1]

BY ETHELDA J. NORBERG, IRVING AUERBACH[2] AND R. M. HIXON

Several investigators have attempted, by chromatographic techniques, the quantitative separation of the ultimate hydrolysis products of methylated starch: i. e., 2,3-dimethyl glucose,

2,3,6-trimethyl glucose, and 2,3,4,6-tetramethyl glucose. Mertzweiller, Carney and Farley[3] separated a synthetic mixture of the pure sugars by conversion to their colored azoyl esters and adsorption on a silica column. Jones[4] hydrolyzed methylated starch with methyl-alcoholic hydrogen chloride to give the tri- and tetramethyl methyl glucosides, which were adsorbed on an alumina column. By analysis of successive portions of the eluate, he showed that these glucosides could be quantitatively eluted in separate fractions.

This laboratory has applied the chromatographic method directly to the methyl glucoses. It was found that ultraviolet light can be used to facilitate the development of such chromatograms, since it permits following visually the separation of the fluorescent glucoses.

When a solution of tri- and tetramethyl glucose in benzene is passed through an alumina column, a single fluorescent band is formed which, upon further development with benzene separates into two bands, the lower being tetramethyl glucose. After forcing the adsorbent out of the tube, the respective bands may be cut from the column and the sugars extracted with methanol. Evaporation of the methanol solution has given a quantitative recovery (95–105%) of the tri- and tetramethyl glucoses.

Since dimethyl glucose is not soluble in benzene, it was separated as follows: A solution of di-, tri- and tetramethyl glucose in acetone–benzene (1:1) was passed through an alumina column and developed with benzene. The dimethyl glucose was adsorbed as a fluorescent band, while the other two sugars passed through unadsorbed. They were recovered by evaporation of the solvent, redissolved in benzene, and separated as described above. The separation of dimethyl glucose from the tri- and tetramethyl glucoses has as yet been carried out only on a qualitative basis, since it was necessary to discontinue the work temporarily.

Experimental

Fibrous alumina was prepared and activated according to the Wislicenus method.[5] It is only faintly fluorescent, while all available commercial alumina preparations proved to be highly fluorescent. The adsorption tubes were 7-inch lengths of 8-mm. Pyrex tubing. A mercury vapor lamp with suitable filter provided a source of ultraviolet light. Since the columns were packed and developed under a constant air pressure (25 cm.), a convenient apparatus for adding the solutions without interrupting the pressure was devised.

In most cases, the following procedure was found satisfactory. The fibrous alumina was made into a thick slurry with benzene and poured into the adsorption tube containing a cotton plug at the bottom. The column was packed by application of pressure to give a 10-cm. length of adsorbent, care being taken not to let it become free of solvent at any time. About 20–50 mg. of the mixed tri- and tetramethyl glucoses, dissolved in 5–10 ml. of warm

(3) Mertzweiller, Carney and Farley, THIS JOURNAL, **65**, 2367 (1943).

(4) Jones, *J. Chem. Soc.*, 333 (1944).

(5) As described in Strain's "Chromatographic Adsorption Analysis." Interscience Publishers, New York, N. Y., 1942, p. 54.

benzene and cooled, was passed through the column. Development with benzene was then begun and continued until the desired separation of bands was obtained. The tube was occasionally moved to a dark box for observation of the fluorescent bands under ultraviolet light. The recovered methyl glucoses were identified by their methoxyl contents and melting points.

The 2,3-dimethyl glucose used in these experiments was obtained through the courtesy of Drs. Coleman and McCloskey at the State University of Iowa.

Aryl Sulfides and Sulfones Containing the Diethylaminoethyl Group

BY B. PUETZER[1] AND A. R. SURREY

Several aryl sulfides and sulfones containing the 4-β-diethylaminoethylamino group have been prepared for the purpose of testing their activity against certain organisms. It has been found that they have only a slight bacteriostatic action *in vitro* against *Staph. aureus*. Similar tests against various intestinal bacilli demonstrated that 4-(β-diethylaminoethylamino)-phenyl 4-nitrophenyl sulfone has definite antibacterial activity toward several members of this group.[2] However, *in vivo* tests showed the compound to be quite toxic to mice.

Experimental

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfide (I).—Forty-six grams of β-diethylaminoethyl chloride and 75 g. of 4-nitrophenyl 4-aminophenyl sulfide[3] were heated with stirring in 150 ml. of nitrobenzene at 120–130° for six hours. The nitrobenzene was removed by steam distillation and the residue was treated with a small amount of ether. On stirring, a solid separated which was filtered off; the yield was 32 g. (30%). Several recrystallizations from alcohol gave yellow plates melting at 89°.

Anal. Calcd. for $C_{18}H_{23}N_3O_2S$: N, 12.17. Found: N, 12.28.

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfide Dihydrochloride.—Alcoholic hydrogen chloride was added to a solution of the base (I) in acetone. Addition of dry ether caused precipitation of the dihydrochloride. It was recrystallized several times from acetone-ether. A light yellow powder was obtained melting at 140–142°.

Anal. Calcd. for $C_{18}H_{25}N_3O_2Cl_2S$: N, 10.05; Cl, 17.0. Found: N, 10.18; Cl, 16.6.

4-(β-Diethylaminoethylamino)-phenyl 4-Aminophenyl Sulfide.—Thirty-two grams of the base (I) was refluxed for three hours in a well-stirred suspension of 120 g. of iron filings in 540 ml. of 50% alcohol containing 3 ml. of acetic acid. The hot reaction mixture was made alkaline with sodium carbonate and filtered. The alcohol was distilled from the colorless filtrate under reduced pressure and the residue was extracted with ether. After removing the ether, the amine was distilled; yield, 7.5 g.; b. p. 234° (1 mm.).

Anal. Calcd. $C_{18}H_{25}N_3S$: N, 13.33. Found: N, 13.33.

(1) Present address: Vick Chemical Co., New York, N. Y.

(2) Our thanks are due to Dr. C. A. Lawrence and G. R. Goetchius for this report.

(3) Gabel and Grinberg, *C. A.*, **34**, 6244 (1940).

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfoxide Hydrochloride.—A solution of 3 g. of the base (I) in 50 ml. of glacial acetic acid and 1.5 ml. of 30% hydrogen peroxide was allowed to stand for twenty-four hours and was then heated on a steam-bath for thirty minutes. The reaction mixture was made alkaline with sodium hydroxide and extracted with ether. After drying and removing the ether, the residual oil was dissolved in absolute alcohol and treated with alcoholic hydrogen chloride; dry ether was then added to turbidity. On standing in the refrigerator an orange powder separated; yield, 1.7 g. After several recrystallizations from alcohol-ether, a product melting at 157–159° was obtained.

Anal. Calcd. for $C_{18}H_{24}N_3O_3ClS$: N, 10.56; Cl, 8.93. Found: N, 10.58, 10.34; Cl, 8.90, 9.06.

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfone (II).—Sixty grams of β-diethylaminoethyl chloride and 28 g. of 4-nitrophenyl 4-aminophenyl sulfone was heated with stirring in 150 ml. of nitrobenzene at 120–130° for eight hours. The nitrobenzene was removed by steam distillation and the residue was made alkaline with sodium hydroxide and extracted with ether. The ether was dried and removed by distillation. The thick oily residue solidified on standing; yield 13.5 g. (35%). After several recrystallizations from alcohol, the sulfone was obtained in the form of light-yellow needles melting at 109°.

Anal. Calcd. for $C_{18}H_{23}N_3O_4S$: N, 11.14. Found: N, 11.18.

4-(β-Diethylaminoethylamino)-phenyl 4-Nitrophenyl Sulfone Hydrochloride.—A solution of II in ether was treated with alcoholic hydrogen chloride. The yellow solid which precipitated was recrystallized from absolute alcohol giving a product which melted at 190–192°.

Anal. Calcd. for $C_{18}H_{24}N_3O_4ClS$: N, 10.16; Cl, 8.58. Found: N, 10.42; Cl, 8.4.

RESEARCH LABORATORIES OF
WINTHROP CHEMICAL COMPANY, INC.
RENSSELAER, NEW YORK RECEIVED NOVEMBER 11, 1944

The Phenylhydrazone Hydrochloride and Some Substituted Phenylhydrazones of *d*-3-Methylcyclopentanone

BY G. H. STEMPEL, JR., W. O. FORSHEY, JR., AND GERSON S. SCHAFFEL

A survey of the literature has revealed that no phenylhydrazone of 3-methylcyclopentanone has been reported. It was therefore with some surprise that a white, crystalline precipitate was observed to form in a polarimeter tube in which the rate of the reaction of *d*-3-methylcyclopentanone with phenylhydrazine, in the presence of excess phenylhydrazine hydrochloride, was being studied by the method of Orning and Stempel.[1] Upon examination the precipitate proved to be the hydrochloride of *d*-3-methylcyclopentanone phenylhydrazone, the positive ion necessary for its formation resulting from the removal of a proton from the phenylhydrazonium ion by the phenylhydrazone. Attempts to prepare the phenylhydrazone itself from the salt were unsuccessful since the phenylhydrazone appears to be too unstable to handle, decomposing spontaneously and rapidly to give a tarry liquid. The hydrochloride is moderately stable when kept in contact with dilute hydrochloric acid solution, but decomposes slowly when dry.

(1) Orning and Stempel, *J. Org. Chem.*, **4**, 410 (1939).

A number of substituted phenylhydrazines were allowed to react with *d*-3-methylcyclopentanone, including the *p*-methoxy-, *p*-bromo-, *p*-nitro- and 2,4-dinitrophenylhydrazines. Of these only the *p*-nitro- and 2,4-dinitrophenylhydrazines yielded stable hydrazones.

Experimental

d-3-**Methylcyclopentanone.**—This compound was prepared from *d*-pulegone by the following steps: (1) hydrolysis of *d*-pulegone to *d*-3-methylcyclohexanone by the method of Wallach[2]; (2) oxidation of the *d*-3-methylcyclohexanone to *d*-β-methyladipic acid by the method of Hartman[3]; and (3) cyclization of *d*-β-methyladipic acid, recrystallized several times from petroleum ether, to *d*-3-methylcyclopentanone by distilling with barium hydroxide according to the method of Thorpe and Kon.[4] The *d*-3-methylcyclopentanone prepared in this way had the following properties: b. p. 145° corrected to 760 mm., $[\alpha]^{27}D$ 153.28°, $[\alpha]^{27}_{5461}$ 190.98°, $n^{27}D$ 1.4282. The rotation of this preparation agrees well with that reported by Godchot, *et al.*,[5] for a sample prepared by cyclizing β-methyladipic acid with acetic anhydride: $[\alpha]^{20}D$ 152.84°, $[\alpha]^{20}_{5461}$ 188.88°, which in turn is considerably higher than rotations, $[\alpha]D$, reported by Zelinsky[6] (135.9°), Wallach[7] (132.96°), and Richaud[5] (130.09°). Godchot[5] reported that the *d*-3-methylcyclopentanone formed by cyclization of his *d*-β-methyladipic acid by distilling with barium carbonate, instead of acetic anhydride, had a rotation of only 146.30°, indicating that partial racemization had occurred during the cyclization. It appears that no racemization took place during the cyclization using barium hydroxide reported here.

d-3-**Methylcyclopentanone Phenylhydrazone Hydrochloride.**—To a mixture of 1 ml. (approx. 0.01 mole) each of phenylhydrazine and *d*-3-methylcyclopentanone was added 1–2 drops of glacial acetic acid. The mixture was kept at or below room temperature by cooling. After five to ten minutes 5 ml. of 1:10 hydrochloric acid was added, followed by enough 95% alcohol (5–10 ml.) to bring about complete miscibility. Then 10 ml. of ether and 2 ml. of concentrated hydrochloric acid were added. When the solution was allowed to evaporate at room temperature, glistening white needles of the hydrochloride separated. The product was then filtered off, washed quickly with alcohol, then ether, and dried in a vacuum desiccator. It had no definite melting point, rapid decomposition beginning at 35–40°. The yield varied from 0.5 to 0.7 g. in different runs.

Anal. Calcd. for $C_{12}H_{17}N_2Cl$: C, 64.13; H, 7.63. Found: C, 64.21; H, 7.48.

The hydrochloride decomposed rapidly enough when dry so that all weighings for analyses had to be made in sealed tubes. The salt-like nature of the hydrochloride was shown by its instantaneous reaction in aqueous solution with silver nitrate to precipitate silver chloride and by the determination of its neutral equivalent by titration with standard sodium hydroxide. Calcd.: neutral equivalent, 224.74. Found: neut. equiv., 226 and 227.

Substituted Phenylhydrazones of *d*-3-Methylcyclopentanone.—The *p*-nitrophenylhydrazone, yellow needle, melting at 155°, and the 2,4-dinitrophenylhydrazones orange needles melting at 144.5–145.5°, were prepared by the methods given by Shriner and Fuson.[8] The melting

(2) Wallach, *Ber.*, **28**, 1965 (1895).

(3) W. W. Hartman, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 19, Note 1.

(4) Thorpe and Kon, *ibid.*, p. 192.

(5) Godchot, Cauquil and Calas, *Bull. soc. chim.*, [5] **6**, 1357 (1939).

(6) Zelinsky, *Ber.*, **35**, 2489 (1902).

(7) Wallach, *ibid.*, **29**, 2965 (1896).

(8) Shriner and Fuson, "Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 142–143.

point of the *p*-nitrophenylhydrazone was depressed by the addition of pure *p*-nitrophenylhydrazine, m. p. 157°.

Anal. Calcd. for the *p*-nitrophenylhydrazone, $C_{12}H_{15}N_3O_2$: C, 61.78; H, 6.49. Found: C, 61.76; H, 6.48. Calcd. for the 2,4-dinitrophenylhydrazone, $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07. Found: C, 51.82; H, 4.81.

Attempts to prepare the *p*-methoxy- and *p*-bromophenylhydrazones by similar methods were not successful.

The authors are indebted to Miss Joy Swan for some of the analyses.

DEPARTMENT OF CHEMISTRY
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           RECEIVED NOVEMBER 24, 1944

Condensation of Chloromaleic Anhydride with Substituted Propenylbenzenes

BY MARTIN E. SYNERHOLM

The condensation of maleic anhydride with iso-safrole to form 6,7-methylene-dioxy-3-methyl-1,2,3,4,-tetrahydronaphthalene-1,2-dicarboxylic acid anhydride has been reported by Hudson and Robinson.[1] They similarly condensed iso-safrole with ethyl acetylenedicarboxylate, obtaining the corresponding 3,4-dihydronaphthalene derivative as the acid anhydride, m. p. 178°.

The latter compound has now been shown to form when chloromaleic anhydride is heated in xylene with isosafrole. Analogous compounds formed when chloromaleic anhydride was condensed with isoeugenol and 2-ethoxy-4-propenylphenol.

Experimental.—The procedures were similar for the three cases. Thirteen grams of chloromaleic anhydride, 15 g. of the propenyl compound, and 50 ml. of xylene were refluxed for six hours. The color turned to a bright red and hydrogen chloride was eliminated during the reaction. On cooling, the products crystallized from the xylene. The yields and properties are tabulated.

DERIVATIVES OF 3-METHYL-3,4-DIHYDRONAPHTHALENE-1,2-DICARBOXYLIC ACID ANHYDRIDE

Derivative	Yield, g.	Solvent	M. p., °C.	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
6,7-Methylenedioxy	10	Benzene	176–177	$C_{14}H_{10}O_5$	65.1	65.0	3.91	3.95
6-Methoxy-7-hydroxy	9	Xylene	225–226	$C_{14}H_{12}O_5$	64.7	65.0	4.65	4.69
6-Ethoxy-7-hydroxy	6	Toluene	192–196	$C_{15}H_{14}O_5$	65.7	65.6	5.14	5.07

Analyses,[2] %

(1) Hudson and Robinson. *J. Chem. Soc.*, 715 (1941).

(2) Analyses by Elisabeth Heber-Smith.

BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.
YONKERS 3, NEW YORK   RECEIVED NOVEMBER 7, 1944

COMMUNICATIONS TO THE EDITOR

TRIFLUOROACETIC ACID AS A CONDENSING AGENT

Sir:

I wish to report the use of trifluoroacetic acid as an agent for the condensation of acetic anhydride with anisole to produce *p*-methoxyacetophenone. The reaction proceeds well (63%, or 91% if allowance is made for recovered anisole) at moderate temperatures (60–70°). Trifluoroacetic acid has several advantages over other reagents commonly employed for such condensations: there is no demethylation of anisole or the product; there is little if any heat of reaction so that all reagents may be mixed at one time; no stirring is required; no corrosive gases are used or formed; the trifluoroacetic acid may be recovered.

Procedure.—On mixing 15 g. of anisole, 14.8 g. of anhydrous trifluoroacetic acid, and 27 g. of acetic anhydride, heat (of mixing) was evolved and a pink color was produced. On warming to 60–70° the color deepened into cherry red. After six hours at 60–70° the mixture was poured into water. The acids were removed by shaking with water and the organic layer was extracted with alkali, but no phenol or *p*-hydroxyacetophenone was found. On vacuum distillation there were isolated 4.7 g. (31%) of anisole and 13.1 g. (63%) of *p*-methoxyacetophenone, b. p. 134–137 at 15–16 mm. This material crystallized and melted over the range 30–36°. The crude semicarbazone formed in 76% yield melted at 193–195°. On recrystallization it melted at 195.6–197.0° cor. These facts indicate that almost pure para derivative was produced.[1] The mixed melting point with purified semicarbazone from commercial *p*-methoxyacetophenone (Eastman Kodak Co.) was not depressed. In a similar experiment, except that the reaction was carried out at 110–125°, a much smaller yield of ketone was obtained as tars were formed.

I have also used trichloroacetic acid[2] in a similar manner, but it is less desirable than trifluoro-

(1) Wahl and Silberzweig. *Bull. soc. chim.*, [4] **11**, 69 (1912), give 36°, 197°, of 138–139° as melting points of ketone and semicarbazone and boiling point of ketone at 15 mm.

(2) Unger, *Ann.*, **504**, 269 (1933).