When another sample of the ethane was heated for the same length of time and then shaken with 40% sodium amalgam for four hours, no red color developed, showing the absence of the starting material.

Three runs of the ethane were prepared from 4 g. of dicyclohexylphenylchloromethane. The solutions of hydrocarbon in ether were allowed to stand for different times and then treated with 40% sodium amalgam and the amount of dicyclohexylphenylacetic acid which could be isolated was noted. One sample was treated at once with amalgam and from it 0.32 g. of the acid was isolated. The second solution stood in the light for eight hours before the amalgam was added. It yielded only 0.12 g. of acid. The third solution stood in the light for five days before the amalgam was added. The amount of acid formed was too small to isolate and weigh. Several other solutions of the hydrocarbon were allowed to stand in the light and some in the dark. The hydrocarbon apparently decomposed rather rapidly in either case.

Summary

1. Dicyclohexylphenylchloromethane has been found to react with 40% sodium amalgam to give sodium dicyclohexylphenylmethyl and a hydrocarbon, $C_{38}H_{54}$.

2. Sodium dicyclohexylphenylmethyl when treated with tetramethylethylene bromide gave tetracyclohexyldiphenylethane. This hydrocarbon absorbed oxygen to give a peroxide and was cleaved by 1% sodium amalgam, indicating that it dissociated to some extent into a free radical.

3. Solutions of tetracyclohexyldiphenylethane were not colored. When the hydrocarbon was heated in solution it rearranged at least in part to the same hydrocarbon that was obtained by the action of sodium amalgam on dicyclohexylphenylchloromethane. The ethane decomposed fairly rapidly at ordinary temperatures.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

CONDENSATION OF 3-PHENYL-2,4-THIAZOLIDIONE WITH AROMATIC ALDEHYDES[1]

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It has long been known that heterocyclic compounds containing the linkage —SCH_2CO— undergo condensation with aromatic aldehydes[3] and with substances like phthalic anhydride and nitrosodimethylaniline,[4] isatin,[5]

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[1] Presented in abstract before the Organic Division at the Columbus meeting, April, 1929.

[2] Part II of the Ph.D. dissertation of Klare S. Markley, June, 1929.

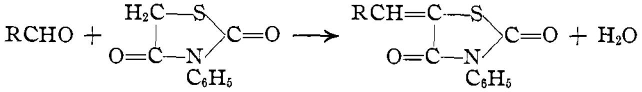
[3] Nencki, *Ber.*, **17**, 2277 (1884); Andreasch, *Monatsh.*, **8**, 407 (1887); Hann and Markley, *J. Wash. Acad. Sci.*, **16**, 169 (1926); Kingsbury and Markley, *ibid.*, **18**, 558 (1928).

[4] Kučera, *Monatsh.*, **35**, 137 (1914).

[5] Andreasch, *ibid.*, **38**, 135 (1917).

alloxan[6] and phenanthraquinone.[7] The reaction conditions and the ease with which condensation occurs depend on the substituents in the heterocyclic ring and upon the nature of the oxygen-containing compound with which it reacts. Among the substances containing the above-mentioned linkage is 3-phenyl-2,4-thiazolidione, which is particularly reactive with aromatic aldehydes.

Ruhemann[8] condensed benzaldehyde, salicylaldehyde, cinnamic aldehyde and piperonal with it, employing alcohol as the solvent and piperidine as catalyst. Andreasch[9] condensed the first two of these aldehydes employing glacial acetic acid as solvent and anhydrous sodium acetate as a dehydrating agent. Since condensation occurs as a result of the splitting out of water between the methylene hydrogen of the parent substance and oxygen of the aldehyde in accordance with the equation



it is obvious that the latter method is preferable.

In view of the fact that the reaction between 3-phenyl-2,4-thiazolidione and aromatic aldehydes takes place readily and smoothly with the formation of easily isolable, stable crystalline products, a number of condensations were carried out to determine the applicability of the method for the characterization of individual members of this class of compounds.

TABLE I

3-PHENYL-2,4-THIAZOLIDIONE CONDENSATION WITH AROMATIC ALDEHYDES

Prepn.	Aldehyde Name	g.	$C_9H_7O_2NS$, g.	CH_3COOH, cc.	Time of reflux, hours	Yield of condensation product g.	%
1	*p*-Tolualdehyde	1.5	2.0	25	5.0	2.2	72
2	*p*-Hydroxybenzaldehyde	3.4	5.0	35	2.0	5.0	65
3	*o*-Chlorobenzaldehyde	3.7	5.0	35	2.25	5.0	61
4	Vanillin	4.0	5.0	35	2.25	5.5	65
5	Veratraldehyde	2.35	2.5	35	2.75	2.0	45
6	Piperonal	3.0	3.0	35	2.50	3.0	59
7	Furfural	3.0	4.0	60	2.0	...	[a]
8	Anisaldehyde	3.0	4.0	35	2.25	4.0	83
9	*o*-Methoxybenzaldehyde	1.5	2.0	25	2.50	2.5	78
10	Benzaldehyde	2.5	4.0	30	2.0	4.0	69
11	Salicylaldehyde	2.7	5.0	30	2.25	3.5	46
12	*m*-Nitrobenzaldehyde	4.0	5.0	40	2.50	3.0	36
13	Cinnamic aldehyde	3.0	4.0	40	3.0	4.5	71

[a] Preparation not weighed; another preparation gave 71% yield.

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[6] Butscher, *Monatsh.*, **32**, 9 (1911).

[7] Raymond M. Hann, Master's thesis, George Washington University, **1926**.

[8] Ruhemann, *J. Chem. Soc.*, **95**, 117 (1909).

[9] Andreasch, *Monatsh.*, **38**, 125 and 127 (1917).

TABLE II

ANALYSES AND PHYSICAL CHARACTERISTICS OF THE ALDEHYDE CONDENSATION PRODUCTS

Prepn.	Condensation product	Physical appearance	Formula	Weight, g.	Nitrogen-K. G. A. method $N/14$ H_2SO_4 consumed, cc.	Nitrogen, % Found	Calcd.	M. p., °C.
1	5-*p*-Tolual-3-phenyl-2,4-thiazolidione	Pale yellow needles	$C_{17}H_{13}O_2NS$	0.3205	15.36	4.79	4.75	192
2	5-*p*-Hydroxybenzal-3-phenyl-2,4-thiazolidione	Short, thick lemon-yellow needles	$C_{16}H_{11}O_3NS$	.2575	12.29	4.77	4.71	257.5
3	5-*o*-Chlorobenzal-3-phenyl-2,4-thiazolidione	White, filamentous crystals	$C_{16}H_{10}O_2ClNS$	.2897	13.02	4.49	4.44	169–170
4	5-Vanillal-3-phenyl-2,4-thiazolidione	Bright yellow fragmented plates	$C_{17}H_{13}O_4NS$	.2537	11.09	4.37	4.28	234–235
5	5-Veratral-3-phenyl-2,4-thiazolidione	Long, bright yellow needles	$C_{18}H_{15}O_4NS$	.2843	11.39	4.01	4.10	208–209
6	5-Piperonal-3-phenyl-2,4-thiazolidione	Slender, bright yellow needles	$C_{17}H_{11}O_4NS$	.3407	14.52	4.26	4.31	207–208
7	5-Furfural-3-phenyl-2,4-thiazolidione	White, filamentous crystals	$C_{14}H_9O_3NS$	.2942	15.17	5.16	5.17	218–219
8	5-Anisal-3-phenyl-2,4-thiazolidione	Pale yellow, filamentous crystals	$C_{17}H_{13}O_3NS$	.2975	13.22	4.44	4.50	199–200
9	5-*o*-Methoxybenzal-3-phenyl-2,4-thiazolidione	Pale yellow microcrystalline powder	$C_{17}H_{13}O_3NS$	.2015	8.61	4.27	4.50	138–139
10	5-Benzal-3-phenyl-2,4-thiazolidione	White, microcrystalline powder	$C_{16}H_{11}O_2NS$	.2805	13.59	4.84	4.98	210–211
11	5-Salicylal-3-phenyl-2,4-thiazolidione	Brownish, yellow needles	$C_{16}H_{11}O_3NS$	.2227	10.58	4.75	4.71	235–236
12	5-*m*-Nitrobenzal-3-phenyl-2,4-thiazolidione	Pale yellow, microcrystalline powder	$C_{16}H_{10}O_4N_2S$	.2669	22.70	8.51	8.59	188
13	5-Cinnamal-3-phenyl-2,4-thiazolidione	Brilliant yellow needles	$C_{18}H_{13}O_2NS$	.2535	11.53	4.55	4.56	212–213

Results and Discussion.—Sixteen aromatic aldehydes were condensed with 3-phenyl-2,4-thiazolidione using glacial acetic acid as solvent and anhydrous sodium acetate as the dehydrating agent. Reaction occurred with the formation of well crystallized, stable products in good yield with all except resorcylaldehyde, hydrocinnamaldehyde and 2,4,6-trinitrobenzaldehyde, with which the reaction occurred to some extent but pure compounds were not isolated from the reaction mixtures. Sharp melting points were observed with most of the products although some of them partially sublimed before melting, a behavior which is also characteristic of the parent substance.

The data concerning the reaction conditions, the yield, melting point and nitrogen content of the products are recorded in Tables I and II.

Ruhemann reported the melting points of the benzylidene and salicylidene compounds at 208–209° and 238–239°, respectively, after recrystallization from alcohol; Andreasch gives 239 and 140°, respectively, whereas our compounds after recrystallization from glacial acetic acid melted at 210–211° and 235–236°, respectively.

Experimental

The parent substance, 3-phenyl-2,4-thiazolidione, was prepared by refluxing thiocarbanilide and monochloro-acetic acid for five hours in glacial acetic acid solution in accordance with the procedure described in a previous paper.[10]

The aldehyde condensations were carried out by dissolving 2 to 5 g. of 3-phenyl-2,4-thiazolidione together with slightly more than the theoretical amount of the appropriate aldehyde, in 25 to 40 cc. of glacial acetic acid containing 5 g. of anhydrous sodium acetate and heating under a reflux condenser for one and one-half to five hours. The reaction product upon cooling almost always solidified in a characteristic crystalline mass. After the addition of water, the mass was disintegrated by shaking, the fine crystalline meal thrown on a Büchner funnel, thoroughly washed with water and usually with small amounts of glacial acetic acid, 50% alcohol and again with water to insure complete removal of the sodium acetate and excess aldehyde. After drying and determining the crude yields, the compounds were recrystallized from glacial acetic acid.

The nitrogen determinations were carried out in accordance with the usual Kjeldahl–Gunning–Arnold procedure except that boric acid[11] was substituted for standard alkali for the absorption of the evolved ammonia, which was then directly titrated with $N/14$ sulfuric acid.

An electrically heated melting point apparatus and Wheeler completely immersed thermometers, standardized by the U. S. Bureau of Standards, were used in determining the melting points of the compounds. They were usually immersed at a temperature approximately 10° below the roughly determined melting point and the temperature was allowed to rise slowly to the observed melting point.

Summary and Conclusions

Thirteen aromatic aldehydes were condensed with 3-phenyl-2,4-thiazolidione and the products isolated and described. The physical appearance, melting point and nitrogen analysis of the resulting product are sufficiently distinctive to warrant the use of the method for the characterization of aromatic aldehydes.

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[10] Markley and Reid, THIS JOURNAL, **52**, 2137 (1930).

[11] Markley and Hann, *J. Assn. Off. Agri. Chem.*, **8**, 455 (1925).