The *threo-t*-butyl 2,3-diphenylbutanoate (white cubes) melted at 99–100.5°.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.92; H, 8.02.

A mixture of the *threo* isomer and the *erythro* isomer (m.p. 136–136.5°) melted at 88–104°. Hydrolysis of 0.2 g. of *threo-t*-butyl 2,3-diphenylbutanoate by the dioxane–hydrochloric acid method (see preceding section) yielded *threo*-2,3-diphenylbutanoic acid (94%), m.p. 134–136° (see Table IV for literature melting point and reference).

Failure of *threo-t*-Butyl 2,3-Diphenylbutanoate to Undergo Epimerization in Liquid Ammonia. (A) With Sodio *t*-Butyl Phenylacetate.—To a stirred suspension of 0.01 mole of sodium amide in 100 ml. of liquid ammonia was added 1.41 g. (0.01 mole) of *t*-butyl phenylacetate in 10 ml. of dry ether, followed, after 15 min., by 0.053 g. (1.79 mmoles) of finely powdered *threo-t*-butyl 2,3-diphenylbutanoate (washed in with 5 ml. of dry ether). After stirring for 2 hr., the reaction mixture was neutralized with ammonium chloride, and the ammonia was replaced with ether. The resulting ethereal suspension was worked up as described before for the alkylations of ethyl and *t*-butyl phenylacetates. The residue left after removal of the solvent from the dried ethereal solution was distilled *in vacuo* to remove the *t*-butyl phenylacetate. Recrystallization of the pot residue from methanol-water yielded *threo-t*-butyl 2,3-diphenylbutanoate, m.p. 91–94°. Upon admixture with an authentic sample (m.p. 96–98°) it melted 94–97°. None of the *erythro* isomer (m.p. 136–136.5°) was found.[23]

(B) With Sodium Amide.—To a stirred suspension of 0.609 mmole of sodium amide in 100 ml. of liquid ammonia was added 0.1504 g. (0.501 mmole) of *threo-t*-butyl 2,3-diphenylbutanoate in 10 ml. of dry ether. After stirring for 2 hr., the reaction mixture was worked up as described before for the alkylation of ethyl and *t*-butyl phenylacetates. Removal of the solvent from the dried ethereal solution of the product gave a residue which was crystallized from methanol-water to yield 0.0726 g. (48%) of recovered *threo-t*-butyl 2,3-diphenylbutanoate, m.p. 92–96°. Upon admixture with an authentic sample (m.p. 96–98°) it had m.p. 94–97°. None of the *erythro* isomer (m.p. 136–136.5°) was found.[23]

Alkylation of Phenylacetic Acid. (A) With β-Phenylethyl Chloride.—To a green stirred suspension of 0.05 mole of disodiophenylacetate (VI), prepared from 0.1 mole of sodium amide and 6.81 g. (0.05 mole) of solid phenylacetic acid in 250 ml. of liquid ammonia, was added 7.03 g. (0.05 mole) of β-phenylethyl chloride in 25 ml. of dry ether. After 1 hr., the reaction mixture was neutralized with ammonium chloride and the ammonia replaced with ether. The resulting ether suspension was extracted twice with 5% sodium hydroxide solution and after addition of a few crystals of hydroquinone, the ethereal solution was dried over anhydrous magnesium sulfate. A portion of the solvent was removed and the solution was chilled, followed by the addition of a slight excess of 10% bromine–carbon tetrachloride solution. The excess bromine was decomposed with 10% sodium bisulfite solution and the layers were separated. The organic layer was washed with 10% sodium bisulfite solution and water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue recrystallized from ethanol–water to yield 2.36 g. (13%) of styrene dibromide, m.p. 71–72° (lit.[24] m.p. 72–73°).

The alkaline extract of the reaction product mentioned before was worked up as described previously to give recovered phenylacetic acid (33%) and 2,4-diphenylbutanoic acid (39%).[9]

(B) With β-Phenylethyl Bromide.—The alkylation was performed as described above, except that 9.26 g. (0.05 mole) of β-phenylethyl bromide was used. The ethereal layer was worked up to yield 12.24 g. (67%) of styrene dibromide, m.p. 72–73.5°, after crystallization from ethanol–water. The yield of 2,4-diphenylbutanoic acid was less than 11%.

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[23] Since the *erythro* isomer is less soluble than the *threo* isomer in the solvent system employed, any *erythro* isomer present should have precipitated as the first crop.

[24] C. R. Hauser, J. C. Shivers, and P. S. Skell, *J. Am. Chem. Soc.*, **67**, 409 (1945).

Ethylenediketene Dimer

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The ethylenediketene dimer obtained from the dehydrochlorination of adipyl dichloride has been reinvestigated and assigned the structure IV. Products derived from this dimer by hydrolysis and oxidation have been identified. The pertinence of this structural information to modes of reaction of alkylketenes is discussed.

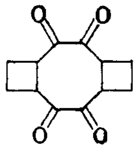
In 1912, Staudinger announced Wedekind's discovery that adipyl dichloride reacts with triethylamine to give a $C_{12}H_{12}O_4$ compound, corresponding to a dimer of ethylenediketene (I).[1] Thirteen years later, Wedekind and co-workers published the details of this reaction and of their attempts to determine the structure of the

$$O{=}C{=}CH{-}CH_2CH_2{-}CH{=}C{=}O$$

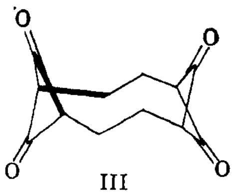
I

dimer.[2] The $C_{12}H_{12}O_4$ compound, m.p. 141–142°, reacted with phenylhydrazine to give a bisphenylhydrazone, with alkaline peroxide to give both a diacid of m.p. 170–171° ($C_{10}H_{14}O_4$) and an acidic substance of m.p. 81–82° ($C_6H_{10}O_5$)[3], and with aqueous acid to give adipic acid.

Two structures for the dimer (II and III) were suggested for consideration; the biscyclobutanedione III was favored. No attempt was made to assign structures to the diacid of m.p. 170–171° or the acidic substance of m.p. 81–82°.



II



III

Assigning structures to the three compounds, $C_{12}H_{12}O_4$, $C_{10}H_{14}O_4$, and $C_6H_{10}O_5$, appeared difficult. An experimental reinvestigation of these compounds provided new analytical, chemical, and spectral data which were sufficient to resolve the problem.

Results and Discussion

The ethylenediketene dimer was prepared and found to have m.p. 142–144° and the molecular formula C_{12}-

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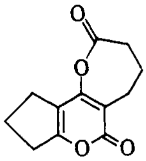
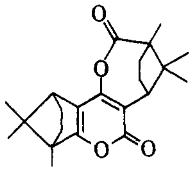
[1] H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 19.

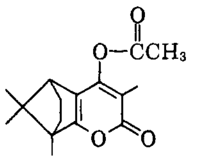
[2] E. Wedekind, M. Miller, and C. Weinard, *J. prakt. Chem.*, [2] **109**, 161 (1925).

[3] There are two apparent misprints in the analytical data reported for the compound of m.p. 81–82° (ref. 2, p. 171); the first sample for combustion is evidently 0.1023 g. rather than 0.1203 g., and the calculated carbon and hydrogen percentages correspond to $C_6H_{10}O_5$, rather than to $C_6H_{10}O_3$ as printed.

$H_{12}O_4$. The structure IV may be assigned to the dimer from a comparison of the ultraviolet and infrared spectral data for the compound [$\lambda_{\max}^{EtOH}$ 313 mμ (ε 7800); $\nu_{\max}^{CH_2Cl_2}$ 1765, 1710, 1640, and 1575 cm.$^{-1}$] with that for V[4] [$\lambda_{\max}^{EtOH}$ 326 mμ (ε 9300); $\nu_{\max}^{CH_2Cl_2}$ 1761, 1692, 1631, and 1565 cm.$^{-1}$] and VI[4] [$\lambda_{\max}^{EtOH}$ 324 mμ (ε 10,500); $\nu_{\max}^{CH_2Cl_2}$ 1773, 1706, 1626, and 1567 cm.$^{-1}$].

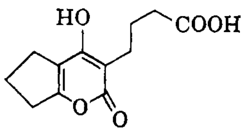

IV


V

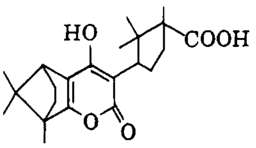

VI

Treatment of the dimer IV with alkaline peroxide according to the procedure of Wedekind and coworkers[2] gave the diacid of m.p. 170–171°. The elemental analysis, molecular weight, and neutralization equivalent of the compound indicated that it was $C_{12}H_{14}O_5$, rather than $C_{10}H_{14}O_4$. Direct hydrolysis of the dimer IV with aqueous sodium hydroxide also gave the diacid, thus confirming that the conversion process is hydrolysis, not oxidation.

The $C_{12}H_{14}O_5$-diacid may be formulated as VII since the infrared spectrum, containing bands at 1707, 1660, 1628, and 1562 cm.$^{-1}$, clearly indicates that the α-pyrone structure of IV survived hydrolysis.[5] The comparable infrared bands at 1689, 1653, 1621, and 1550 cm.$^{-1}$ reported for the acid VIII[4] may be viewed as supporting a similar structural assignment for VII.



VII

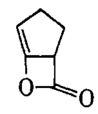


VIII

The acidic substance of m.p. 81–82° was isolated and found to be $C_6H_8O_4$, rather than $C_6H_{10}O_5$. The infrared spectrum of the compound suggested that it might be an impure specimen of glutaric acid and this possibility was confirmed by paper chromatographic analysis. No effort was made to isolate and identify the substance mixed with the glutaric acid.

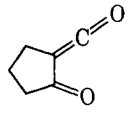
The formation of the dimer IV from the dehydrochlorination of adipyl dichloride is worth comment. Long-chain α,ω-diacid chlorides may be dehydrochlorinated to give materials that probably are β-lactone intramolecular alkylketene dimers.[6] The short-chain α,ω-diacid chlorides do not behave similarly. They give polymers when dehydrochlorinated and left to react in aprotic media[6,7], or, as in the present work, dimers based on an α-pyrone structure.

Two main possibilities may be considered responsible for this diffrence in behavior. It may be that the short-chain α,ω-diacid chlorides cannot give intramolecular ketene condensation products (such as IX from ethylenediketene) for steric reasons; or it may be that a hypothetical intermediate such as X would condense intramolecularly with the nearby ketene function and subsequently eliminate hydrogen chloride to give XI and, eventually, dimers of XI,[8] and a β-lactone is not obtained because an α,ω-diketene is never involved.


IX

$O{=}C{=}CH{-}CH_2CH_2{-}\bar{C}H{-}COCl$

X


XI

Experimental tests of these two rationalizations are now in progress.

Experimental[9]

Ethylenediketene Dimer.[2]—A solution of 105 g. (1.15 equiv.) of adipyl dichloride in 1250 ml. of absolute ether was placed in a dry 2-l. three-necked flask; this flask was equipped with a reflux condenser, mechanical stirrer, addition funnel, nitrogen line, and drying tube. Triethylamine (119 g., 1.17 moles, freshly distilled from α-naphthyl isocyanate) was added to the stirred mixture in an atmosphere of nitrogen during 70 min. Three days later the ethereal solution from the reaction was separated from insoluble polymer and salt by inverted filtration and concentrated to give a colorless solid. Two recrystallizations from benzene gave the ethylenediketene dimer of m.p. 142–144° (lit.[2] m.p. 141–142°) (2.8 g., 4.4% yield).

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49; mol. wt., 220. Found: C, 65.22; H, 5.51; mol. wt., 215.

The compound had n.m.r. absorptions only in the region between 110 and 190 c.p.s. below tetramethylsilane and $\lambda_{\max}^{EtOH}$ 313 mμ (ε 7800); $\nu_{\max}^{CH_2Cl_2}$ (selected) 1765, 1710, 1640, 1575, 1370, 1225, 1195, 1110, 1070, 1050, 1035, and 965 cm.$^{-1}$.

Hydrolysis Product from Ethylenediketene Dimer.—The dimer of m.p. 142–144° (583 mg.) was covered with 5 ml. of water and treated with 1.43 g. of sodium peroxide according to the method of Wedekind, *et al.*[2] Acidification of the reaction mixture gave a colorless solid which was recrystallized from water to afford 283 mg. (45%) of hydrolysis product having m.p. 168–170°. The analytical sample had m.p. 169.5–171° (lit.[2] m.p. 170–171°), $\lambda_{\max}^{EtOH}$ 298 mμ (ε 11,400), shifted to 292 mμ on addition of sodium hydroxide; $\nu_{\max}^{KBr}$ (selected) 1707, 1660, 1628, and 1562 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92; mol. wt., 238; neut. equiv., 119. Found: C, 60.48; H, 5.87; mol. wt., 241; neut. equiv., 121.

When 73 mg. of the dimer and 1 ml. of 5% aqueous sodium hydroxide were combined and heated for 40 min. at 80°, a clear solution was obtained which was cooled and acidified to give 83 mg. (105%) of crude diacid, m.p. 169–171°; the infrared spectrum of this material was identical with that of the diacid of m.p. 169.5–171° obtained previously.

Oxidation Product from Ethylenediketene Dimer.—The mother liquor of the acidified reaction mixture from 583 mg. of dimer (IV) and 1.43 g. of sodium peroxide (*cf.* previous section) was extracted ten times with 10-ml. portions of ether. The combined ether extracts were washed once with saturated sodium chloride, dried over calcium sulfate, filtered, and concentrated to

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[4] P. Yates and E. A. Chandross, *Tetrahedron Letters*, No. **20**, 1 (1959); E. A. Chandross and P. Yates, *Chem. Ind.* (London), 149 (1960).

[5] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p. 52.

[6] A. T. Blomquist and R. D. Spencer, *J. Am. Chem. Soc.*, **69**, 472 (1947); **70**, 30 (1948).

[7] For example, see J. C. Sauer, *ibid.*, **69**, 2444 (1947).

[8] See ref. 4, and W. R. Hatchard and A. K. Schneider, *ibid.*, **79**, 6261 (1957).

[9] Melting points are uncorrected. Analyses are by J. Nemeth and associates, Urbana, Ill.

give 191 mg. of colorless crystals, m.p. 80–83° (lit.[2] m.p. 81–82°). Recrystallization from benzene gave material of m.p. 83–84° (partial melt; clear melt at 190°).

Anal. Calcd. for $C_5H_8O_4$: C, 45.45; H, 6.10; neut. equiv., 66. Found: C, 45.73; H, 6.09; neut. equiv., 72.

Examination of this material by infrared spectroscopy and paper chromatography with 1-propanol–concentrated ammonium hydroxide–water (60:20:20 by volume) as developer indicated that it was mostly glutaric acid (R_f 0.52). No acidic impurities were detected by paper chromatography; the infrared spectra of the oxidation product and glutaric acid were similar, but not superimposable.

The Ferric Chloride Oxidation of 5-Substituted *o*-Semidines and the Polarographic Properties of the Products

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Contribution No. 1524 from the Department of Chemistry, University of California, Los Angeles 24, California

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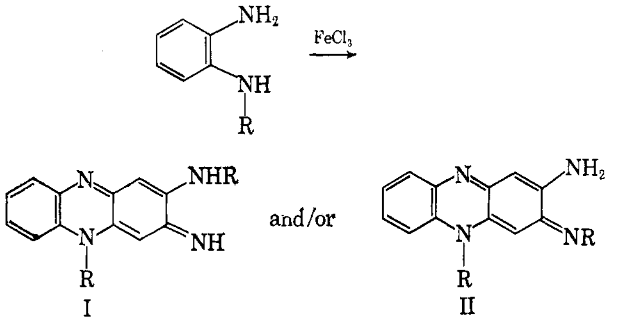
The ferric chloride oxidation of 5-substituted *o*-semidines (2-aminodiphenylamines) yielded 7-substituted 2-amino-3,5-dihydro-5-phenyl-3-phenyliminophenazines as main products, with elimination of one of the 5-substituents of the starting *o*-semidine. Condensation of these phenazine derivatives with ketones led to characteristic Schiff bases. Some polarographic properties of these phenazine derivatives were studied and the effect of substituents on the half-wave potentials was found to be in good agreement with Hammett's σ-values.

The ferric chloride oxidation of mono-*N*-substituted *o*-phenylenediamines has been investigated by Barry *et al.*,[1–3] who have proven that the main oxidation products are phenazine derivatives existing in two isomeric structures I and II which are formed either as a mixture or separately, depending on the nature of the starting amine.



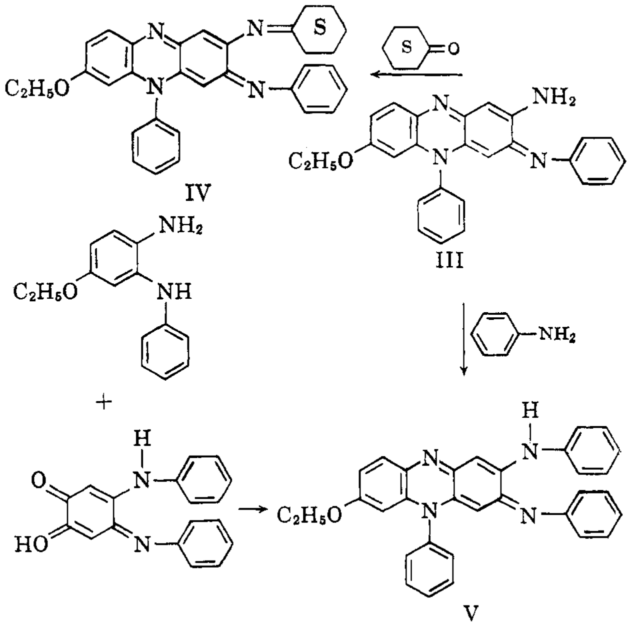
I II

In the oxidation of 2-amino-5-chlorodiphenylamine one chlorine atom is eliminated and only the 7-chloro-II-isomer is formed.

In this laboratory, oxidation products of substituted 2-aminodiphenylamines (*o*-semidines) had been investigated previously as to their suitability as internal indicators in redox titrations. The present paper reports on compounds obtained by the ferric chloride oxidation of some 5-substituted 2-aminodiphenylamines and some of their polarographic properties.

A series of 5-substituted 2-aminodiphenylamines (as the hydrochlorides) were oxidized in aqueous alcoholic solution with ferric chloride. The 5-substituents included various halogen and alkoxy groups. These *o*-semidines were obtained by reduction of the corresponding substituted 2-nitrodiphenylamines, which in turn were prepared by the reaction of substituted anilines with substituted *o*-dinitro- or *o*-halonitrobenzenes. The oxidation products were separated and purified by liquid column chromatography on alumina.

On the basis of the previously cited prior investigations, the deeply colored main oxidation products were expected to be phenazine derivatives with structures analogous to the preceeding I- or II-isomers. This was indeed supported by the elemental analyses of these compounds which also indicated that in each case one of the 5-substituents had been eliminated in the oxidation. Since it seemed not altogether certain whether an alkoxy group would be eliminated in the same fashion as one of the chlorine atoms in the previously mentioned oxidation of 2-amino-5-chlorodiphenylamine, the structure of the main oxidation product of 2-amino-5-ethoxydiphenylamine was determined as 2-amino-3,5-dihydro-7-ethoxy-5-phenyl-3-phenyliminophenazine (III) by the following reactions.



IV III V

Treatment of this oxidation product with aniline (analogous to Barry, *et al.*,[4]) yields compound V, which was independently synthesized by condensation of 2-amino-5-ethoxydiphenylamine with 4,5-dianilino-*o*-quinone. This proved a structure analogous to either

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[1] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *J. Chem. Soc.*, 888 (1956). This paper includes a literature survey of earlier work.

[2] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 893 (1956).

[3] V. C. Barry, J. G. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 896 (1956).

[4] V. C. Barry, J. C. Belton, J. F. O'Sullivan, and D. Twomey, *ibid.*, 895 (1958).