be, there remains the comforting fact that dimethyl-nitrosamine also differs from the effective amide catalysts by being devoid of measurable basicity (Table II, group A).

Dipole Moments and Polarizabilities.—The present work has served to emphasize the primacy of linear π-bond moments (as compared to σ-bond moments) of polar substances in determining their ability to solvate sodium ions in nonpolar media and, consequently, to catalyze the alkylation reaction. Since the observed dipole moment of an unsaturated polar substance is the algebraic sum of its σ- and π-moments, it is not surprising that little connection between dipole moment and catalytic activity can be found. Table IV lists a num-

TABLE IV

DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF RE-
AGENTS

Compound	ϵ	μ, D.
C_6H_6	3	0
C_2H_5Br	9	1.8
$(C_2H_5O)_2CO$	3	0.9
CH_3CN	39	3.2
C_6H_5CN	26	3.9
$(CH_3)_2CO$	21	2.8
$(CH_3)_2NNO$		3.98
$C_6H_5NO_2$	36	4.0
C_2H_5OH	25	1.7
$(CH_3)_2NCON(CH_3)_2$		3.3
$HCON(CH_3)_2$	37	3.82
$CH_3CON(CH_3)_2$	38	3.87
$(CH_3)_2SO$	45	
Pyridine N-oxide		4.28

pinching the triatomic molecular orbital in the middle and of decreasing delocalization of the lone pair of the terminal nitrogen. The energy barrier must then be accounted for by overlap of the two lone pair orbitals and the dipole moment by the atomic dipole of the central nitrogen combined with the dipole of the N–O bond. The nitroso group thus resembles the nitro group of nitrobenzene more than the carbonyl group of an amide.

(37) Compare G. G. Stewart and H. Eyring. *J. Chem. Ed.*, **35**, 550 (1958).

ber of reagents and additives used in this work together with their dielectric constants and dipole moments. As the additives are listed in roughly increasing order of activity, it is easy to see that, while the ineffective compounds may or may not possess strong dipoles, all of the effective additives do. This is compatible with the contention that a certain kind of dipole (due to a linear π-moment) is necessary for catalytic action.

It is well known[38] that separation of charge stiffens or reduces the electron polarizability of a bond. Furthermore, π-electrons are usually more polarizable than σ-electrons and contribute more to the refractivity of an unsaturated group. That the group refractions (electron polarizabilities) of the PO and SO bonds are much smaller than those for the CO and CN groups is further indication that, in the former, the π-orbitals are more polarized in the ground state than they are in the latter. The trend discernible in Table III also betokens a similar variation of π-orbital polarization, roughly related to catalytic activity, within the series of amides. Judging from these observations, then, it appears that the burden of success in solvation rests with the additive. The importance of inductive polarization brought about by proximity of the positive sodium ion must be relatively small. Again, it is the π-electron density in the ground state of the additive that is critically important.[39]

Acknowledgments.—The author is indebted to Mr. Frank Chadde for the ultraviolet spectra, Mr. William Washburn for the infrared spectra, Miss Gwen Prior for the densities and refractive indices and to Mr. David Wimer for the potentiometric titrations.


Cyclopentene-3,5-dione. III. Reactions of the Methylene Group[1,2]

BY C. H. DEPUY AND P. R. WELLS

Reactions of the active methylene group of cyclopentene-3,5-dione are reported. It has proved possible to condense it with benzaldehyde in acid solution, through the intermediacy of β-hydroxy-cyclopentadienone, as well as in basic solution. By reaction with aryldiazonium salts the arylhydrazones of cyclopentene-3,4,5-trione have been prepared. Some studies on the kinetics of the base-catalyzed polymerization of the dione are recorded and a mechanism for the polymerization is suggested.

Cyclopentene-3,5-dione (I) is a stable, highly reactive compound easily prepared by the oxidation of the commercially available diol.[3] Because so little is known about the synthesis and properties of highly unsaturated five-membered ring compounds, and because this enedione contains such a

variety of reactive centers, we have been exploring the synthetic utility of this compound. Reductions, derivatizations and Diels–Alder reactions have already been reported.[1,3] In this paper we describe some reactions of the methylene group.
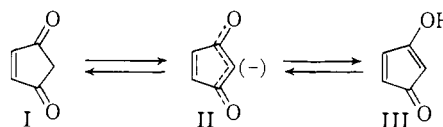

(1) Paper II in this series, C. H. DePuy and C. E. Lyons, THIS JOURNAL, **82**, 631 (1960).

(2) Supported by a grant from the National Science Foundation.

(3) C. H. DePuy and E. F. Zaweski, THIS JOURNAL, **81**, 4920 (1959).

Normal alkylation and condensation reactions of cyclopentene-3,5-dione are made synthetically difficult (and correspondingly interesting from the theoretical standpoint) by two unique aspects of its chemistry. We have already pointed out that the molecule is apparently completely ketonic, the enol form III being unfavorable because of its relationship to cyclopentadienone.[1-3] It was anticipated, then, that acid-catalyzed condensations would be especially difficult. On the other hand, the enedione is exceptionally unstable in base, polymerizing very rapidly under the mildest conditions (vide infra). This fact severely limits this route for the preparation of condensation and alkylation products.

As reasonably typical of aldol condensations, the preparation of the benzylidene compound was extensively investigated (equation 1). If the condensation be attempted in the presence of

$$ \qquad\qquad (1) $$
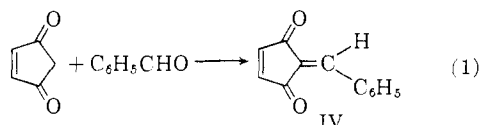
aqueous or alcoholic base,[4] no benzylidene compound is isolated, the only product being polymer from the enedione. Numerous attempts at base-catalyzed reactions led to the same results. We next turned our attention to acid-catalyzed condensations, for we were especially interested in assessing the ease with which the enol form could occur. Surprisingly, only rather mild conditions were required. Thus, a mixture of the dione and excess benzaldehyde in ether containing BF_3, when heated at reflux for one hour, readily formed the yellow, crystalline benzylidene derivative in about 50% yield. Yields were appreciably smaller (25%) when equimolar amounts of dione and aldehyde were used.

Although the BF_3-catalyzed condensation undoubtedly proceeds by way of an intermediate closely resembling the enol form III, the presence of the BF_3 and the use of a non-polar solvent complicate the picture. Consequently, the condensation was investigated under conditions in which the enol itself is a still more likely intermediate. It was found that the benzylidene compound was again formed (in 42% yield) when the dione, an excess of benzaldehyde, and a trace of sulfuric acid were heated under reflux in glacial acetic acid. It seems clear, then, that while the tautomeric hydroxycyclopentadienone form is not stable enought to be observable, it is in ready equilibrium with the dione.[5]
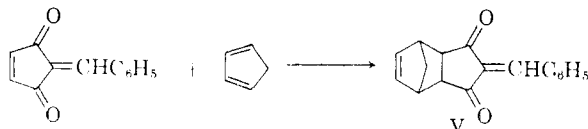
With the success of the acid-catalyzed condensation, we examined more thoroughly condensations catalyzed by bases. It was found that the reaction could be carried out by the use of aprotic solvents and weak bases. Thus, a very small amount (5% yield) of 4-benzylidene-cyclopentene-3,5-dione was obtained using triethylamine in benzene for the base and more reasonable yields (20%) were realized using the pre-formed piperidine

benzaldehyde complex in dry ether.[6] It seems that condensation reactions of cyclopentene-3,5-dione can be successfully carried out, but that the competing polymerization in base makes the acid-catlyzed reactions most promising.

The benzylidene compound displays some interesting reactions in its own right. It undergoes the Diels-Alder reaction readily, although less so than does the dione itself. Thus, when allowed to react with cyclopentadiene in benzene solution at room temperature, it was gradually converted to the adduct V, m.p. 180-181°. This same product was obtained when the adduct of cyclo-
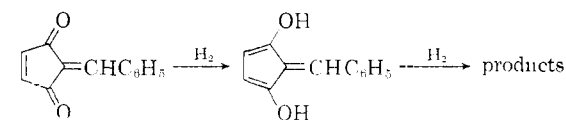
pentene-3,5-dione and cyclopentadiene[3] was condensed with benzaldehyde in alcoholic base. Its structure is also supported by its infrared spectrum, which bears a strong resemblance in the carbonyl region to that of the benzylidene derivative of indane-1,3-dione. The pertinent comparisons are recorded in Table I. The ultraviolet spectrum of the benzylidene compound is shown in Fig. 1.

TABLE I

CARBONYL FREQUENCIES OF CYCLOPENTENE-3,5- AND INDANE-1,3-DIONES

Compound	Cm.$^{-1}$
Cyclopentene-3,5-dione	1748, 1712
Indane-1,3-dione	1750, 1710
4-Benzylidene-cyclopentene-3,5-dione	1748, 1686
2-Benzylidene-indane-1,3-dione	1737, 1696

The benzylidene compound further resembles the corresponding derivative of indan dione in its ready reversion to benzaldehyde and the dione. When an alcoholic solution is made basic, it immediately develops ultraviolet spectrum characteristic of an equimolar mixture of benzaldehyde and polymerized dione. And if the original alcohol solution be treated with 2,4-dinitrophenylhydrazine, benzaldehyde 2,4-DNP is formed in good yield. The compound is, on the other hand, stable to acids and does not react with 2,4-DNPH in acid solution.

Catalytic hydrogenation of the benzylidene compound in ethanol over platinum oxide resembles hydrogenation of the dione itself[3] in that somewhat more than two molar equivalents of hydrogen are absorbed and a complex mixture of products is formed.[7] These products were not investigated

(4) A. I. Vogel, "Elementary Practical Organic Chemistry," Vol. 2, Longmans, Green and Co., London, p. 148.

(5) It should be recalled that cyclopentane-1,3-dione is completely enolic; see ref. 3 for discussion.

(6) N. J. Leonard, J. C. Little and A. J. Kresge, THIS JOURNAL, 79, 6436 (1957).

(7) In this regard it might be pointed out that the benzylidene compound might be considered to be a "phenylfulvene quinone," and that the hydrogenation (and perhaps other reactions) might take place by 1,6-addition.
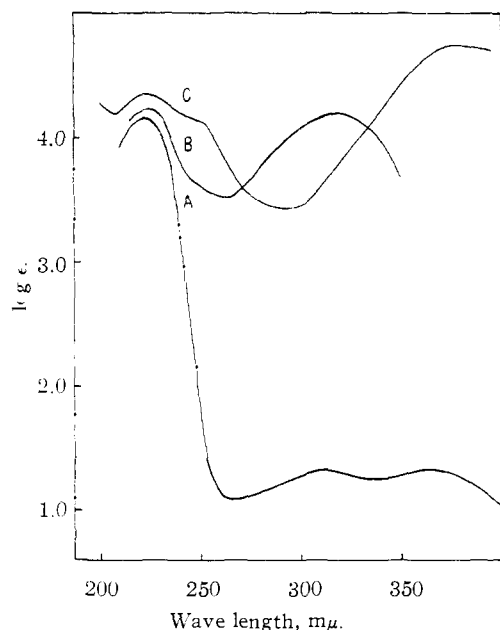
Fig. 1.—Ultraviolet absorption spectra in aqueous ethanol for: (A) cyclopentene-3,5-dione; (B) 4-benzylidene-cyclopentene-3,5-dione; (C) cyclopentene-3,4,5-trione-phenylhydrazone.

Attempts to carry out condensation reactions in basic media with a variety of other compounds, including nitrite esters and acid halides, led only to polymeric material. Obviously self-condensasation is too rapid to allow competition from any but the most reactive substrate. It was reasoned that a diazonium ion might be reactive enough to compete successfully for the enolate ion. That active methylene compounds will react with diazotized aromatic amines has been known since the time of V. Meyer, who treated nitroethane[8] and acetoacetic ester[9] with benzene diazonium salts. The initial products of such reactions, mixed azo compounds, are tautomers of aryl hydrazones, and the tautomerization is generally greatly in favor of the latter.

When an acidic solution of cyclopentene-3,5-dione and benzenediazonium chloride or p-nitrobenzenediazonium sulfate are mixed, no reaction takes place. Addition of sufficient sodium acetate solution to neutralize the acid present gives an immediate precipitate of the 4-phenyl- or 4-p-nitrophenylhydrazone of cyclopentene-3,4,5-trione (VII). Thus the enolate ion has effectively been
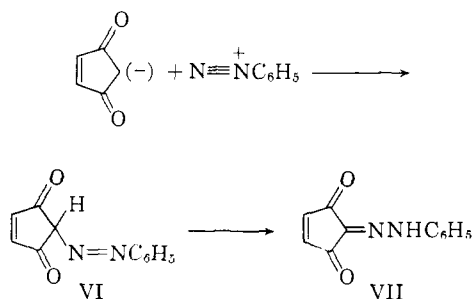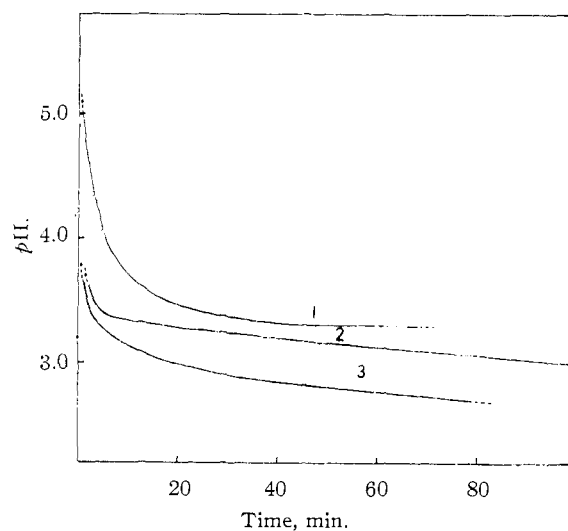

Fig. 2.—Variation of pH of aqueous solutions of cyclopentene-3,5-dione with time: (1) 0.008 M; (2) 0.04 M; (3) 0.1 M.

trapped by a more reactive electrophile than a second dione molecule. The ultraviolet and infrared spectra of the products support the hydrazone structure VII rather than the tautomeric azo structure VI. These hydrazones are soluble in base, forming highly colored anions, and are very unreactive in the Diels–Alder reaction.

Our interest in the parent cyclopentene-3,4,5-trione led us to attempt the hydrolysis of these phenylhydrazones. Under moderate hydrolysis conditions with formaldehyde[10] or levulinic acid[11] the hydrazones were recovered unchanged, and under the drastic conditions necessary to effect any reaction, the hydrolysis products, if any were formed, were not stable. Other approaches to this interesting compound are being explored.

Since the base-catalyzed polymerization interfered so drastically with many reactions of the dione, it seemed pertinent to study it in more detail. When a dilute solution of the dione is treated with base, a red color rapidly develops. Acidification changes the color to yellow, but no dione can be recovered from the solution. Evaporation of the solvent leaves a tan solid, very soluble in water and insoluble in organic solvents. If a concentrated solution of the dione is treated with base, a polymer precipitates which is insoluble in water and organic solvents. When an aqueous solution of the dione is allowed to stand it gradually polymerizes, but it is stable in acid solution.

The rate of polymerization has been followed by two methods. As mentioned above, in water solution the pH of the solution falls (Fig. 2), rapidly at first, then slowly until a constant value is reached and all the dione has polymerized. From the data obtained, it is possible to extrapolate to zero time and estimate, approximately, the initial rate of reaction (Table II). These results, although based on an uncertain extrapolation, suggest that the initial step under these conditions is

(8) V. Meyer, Ber., 8, 751 (1875).

(9) V. Meyer, ibid., 10, 2075 (1877).

(10) Cf. A. Lapworth, J. Chem. Soc., 91, 1133 (1907).

(11) C. H. DePuy and B. W. Ponder, THIS JOURNAL, 81, 4629 (1959).

the ionization of the dione to form the enolate anion. Little information can be derived from the later stages of the reaction where, amongst other complications, the acidity of the medium is changing.

TABLE II

INITIAL RATES OF POLYMERIZATION OF AQUEOUS SOLUTIONS OF CYCLOPENTENE-3,5-DIONE (25°)

[Dione]$_0$	Final pH	$(d[H^+]/dt)_0$, mole l.$^{-1}$ sec.$^{-1}$	$(d[H^+]/dt)_0/$ [dione]$_0$, sec.$^{-1}$ $\times$ 10^4
0.104	2.5	7 $\times$ 10^{-5}	7
.042	2.7	3 $\times$ 10^{-5}	8
.014	3.0	1 $\times$ 10^{-6}	7
.0078	3.2	7 $\times$ 10^{-7}	8

The second method of study was to allow the dione to polymerize in buffered solutions (pH 6.79, 6.97, 7.52 and 7.61) and to follow the rate of destruction of the dione by observing the spectrum of samples quenched in aqueous hydrochloric acid. Reliable results were obtained using the method of Dewar and Urch,[12] especially after the first third of the reaction. Slight broadening of the band due to the polymer, however, reduced the accuracy of the method. Initially the reaction is first order in dione with rate constants of 5–13 $\times$ 10^{-4} sec.$^{-1}$, agreeing well with the values obtained above. The order of the reaction increases with time, its value at any point being dependent also upon the initial dione concentration and the pH.

Comparison of the spectra of the polymer in acidic and basic aqueous solution with those of cyclopentane-1,3-dione under the same conditions indicates that the polymer probably contains the same absorbing system, i.e., α-hydroxycyclopentenone. The following path seems to us to be a reasonable one, with the first step being rate-determining initially, but decreasing in importance as the concentration of dione decreases.

polymer ←
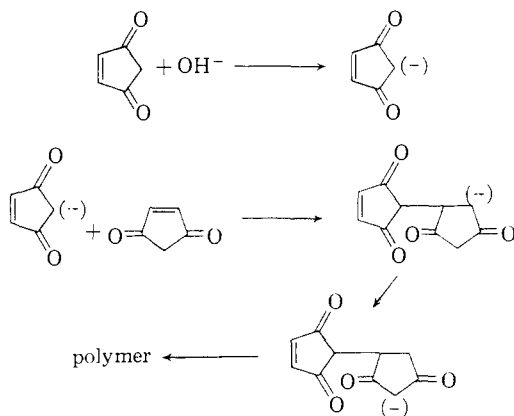
Experimental

All melting points are corrected and were determined using a Fisher–Johns apparatus. Ultraviolet spectra were recorded on a Cary model 14 recording spectrophotometer and infrared spectra on a Perkin–Elmer model 21 spectrophotometer using NaCl prisms. pH measurements were carried out using a Beckman glass electrode pH meter, model H-2. Analyses are by Drs. Weiler and Strauss, Oxford, England, or by Midwest Microlab, Indianapolis, Ind.

(12) M. J. S. Dewar and D. S. Urch, J. Chem. Soc., 345 (1957).

Reaction of Cyclopenten-3,5-dione with Sodium Hydroxide.—The dione (0.5 g., 0.005 mole) in water (5 ml.) was treated with 53 ml. of 0.1 N aqueous sodium hydroxide and stirred for 20 minutes. After passage through Amberlite I.R. 120 ion-exchange resin to remove sodium ions, the red-brown solution was evaporated to dryness at room temperature yielding a tan, highly enolic powder, m.p. > 300°, insoluble in organic solvents but readily soluble in aqueous sodium hydroxide and slowly soluble in water.

Anal. Calcd. for $C_5H_4O_2 \cdot ^2/_3H_2O$: C, 55.55; H, 4.97. Found: C, 55.44; H, 4.87.

Acidification of the above sodium hydroxide solution with 0.5 N aqueous hydrochloric acid yielded a brown colloidal precipitate which rapidly redissolved on basification. After drying at 50°, however, the dark brown powder obtained, m.p. 300°, dissolved only sluggishly in aqueous sodium hydroxide.

Anal. Found: C, 54.6; H, 4.69.

A similar precipitate begins to separate from *ca.* 0.1 M dione solutions in 0.1 N aqueous hydrochloric acid after 7 days at 25°.

In 0.0025 N aqueous hydrochloric acid the dione exhibits a strong absorption maximum at 222 mμ (log ε 4.17), while in 0.0025 N aqueous sodium hydroxide a broader absorption has its maximum at 261 mμ (log ε 4.08). Aqueous solutions initially exhibit only the 222 mμ absorption, but its intensity slowly falls with time while a broadened 261 mμ absorption appears having an ill-defined shoulder at *ca.* 250 mμ. A strongly acidified aqueous sodium hydroxide solution has a maximum at 250 mμ, while weakly acidified aqueous solutions absorb at 222 mμ, with shoulders at *ca.* 250 and *ca.* 260 mμ, the individual intensities and the general absorption pattern depending upon the acidity of the solution and the time it was allowed to stand before acidification.

4-Benzylidene-cyclopenten-3,5-dione. A.—The dione (1 g., 0.01 mole) in anhydrous ether (25 ml.) was treated with a mixture of benzaldehyde (5 ml., *ca.* 0.05 mole) and boron trifluoride ether complex (25 ml.) and the yellow solution was heated at gentle reflux for one hour. After cooling, the resulting solution was thoroughly washed with saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate and evaporated to dryness. Extraction of the yellow semi-solid product with cold pentane removed almost all of the excess benzaldehyde, leaving a yellow product, m.p. 142–144° (1.0 g., 52%). Crystallization from aqueous acetone gave long, pale yellow needles m.p. 146–146.5°; λ$_{max}$ (aqueous ethanol): 319, 224 mμ (log ε 4.24, 4.24); principal infrared bands (CCl$_4$): 1748, 1686, 1620, 1595, 1172, 1167, 1043, 859 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.19; H, 4.29.

Employing only 0.01 mole of benzaldehyde in the above reaction gives a 25% yield of the benzylidene compound and considerable quantity of brown resinous material.

B.—A solution of the dione (0.2 g., 0.002 mole) and benzaldehyde (0.4 ml., *ca.* 0.004 mole) in glacial acetic acid (10 ml.) was treated with three drops of concentrated sulfuric acid and heated under gentle reflux for 2 hours. The cooled solution was diluted with water, thoroughly extracted with methylene chloride, the extracts washed with water, 2% aqueous sodium bicarbonate, saturated sodium chloride solution and dried over anhydrous sodium sulfate. The yellow product obtained after solvent removal was crystallized from aqueous acetone to yield pale yellow needles, m.p. 145–146° (0.155 g., 42%).

C.—The dione (0.5 g., 0.005 mole) was added to a solution of benzaldehyde (1.7 g., 0.016 mole) and piperidine (5 drops) in anhydrous ether (10 ml.). This solution was stirred overnight, during which time a small amount of brown material, m.p. > 300°, separated. The filtered solution on treatment with hexane and cooling deposited yellow material; crystallized from aqueous acetone, m.p. 145–146° (0.2 g., 22%).

D.—The dione (0.2 g., 0.002 mole) was allowed to stand at room temperature in benzene (20 ml.) solution with benzaldehyde (1 ml., 0.01 mole) and triethylamine (0.1 ml.). Within 5 minutes the yellow solution had become brown and after two hours a considerable precipitate of polymer had formed. Evaporation yielded brown material, m.p. > 300°, containing a small amount of yellow product which was

extracted with hot benzene. Crystallization from benzene–hexane gave pale yellow crystals, m.p. 146° (0.02 g., 5%).

No apparent reaction occurs in the absence of base, as evidenced by the recovery of a small amount of unchanged dione. Prolonged heating, however, leads to the formation of polymeric material.

Reaction of the Benzylidene Compound with Sodium Hydroxide.—The benzylidene compound (0.0060 g., 6 × 10^{-5} mole) in 0.04 N sodium hydroxide in 20% v./v. aqueous ethanol (1 l.) has an ultraviolet absorpton maximum at 265 mμ of intensity corresponding to ca. 6 × 10^{-5} M dione polymer; 500 ml. of this solution treated with 500 ml. of 1.0 N aqueous sulfuric acid has absorption maxima at 246 and 250 mμ, with a shoulder at ca. 280 mμ, corresponding to 1–5 × $10^{-5}M$ benzaldehyde and 1–5 × $10^{-5}M$ dione polymer.

The benzylidene compound (0.05 g.) in ethanol (10 ml.) was treated with 0.1 N aqueous sodium hydroxide (10 ml.) followed by an excess of a solution of 2,4-dinitrophenylhydrazine in aqueous hydrochloric acid. Dilution with water gave a red precipitate, which was crystallized from aqueous ethanol to yield orange crystals, m.p. 238°, of benzaldehyde 2,4-dinitrophenylhydrazone.

Reaction of the Benzylidene Compound with 2,4-Dinitrophenyl-hydrazine.—The benzylidene compound (0.06 g.) and 2,4-dinitrophenylhydrazine (0.07 g.) in hot ethanol (10 ml.) were allowed to stand at room temperature for 6 hours. Evaporation yielded red material which was dissolved in hot benzene and chromatographed on alumina to give benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 236–237°. A small amount of the benzylidene compound was also recovered.

Reaction of the Benzylidene Compound with Cyclopentadiene.—The benzylidene compound (0.26 g.) and freshly distilled cyclopentadiene (0.225 ml.) were allowed to stand at room temperature in benzene solution (10 ml.) for 24 hours. Evaporation yielded a yellow liquid product from which cyclopentadiene dimer was extracted with pentane. Crystallization (twice) of the residue from benzene yielded white needles, m.p. 180° (0.20 g., 57%), undepressed by admixture with the product obtained (in moderate yield) by the reaction of benzaldehyde with the cyclopentadiene adduct of the dione in aqueous ethanolic sodium hydroxide; principal infrared bands (CHCl₃): 1675, 1618, 1397 cm.⁻¹.

Reaction of the Dione with Diazotized Aniline.—Aniline hydrochloride (6.5 g., 0.05 mole) was dissolved in hot water

(25 ml.) containing concentrated hydrochloric acid (6 ml.), cooled in ice and treated with sodium nitrate (3.65 g.) dissolved in the minimum of water. This solution after standing for 30 minutes was treated with a further 25 ml. of water, mixed with a solution of the dione (3.85 g., 0.04 mole) in water (50 ml.) and treated with excess of a saturated aqueous solution of sodium acetate. A yellow precipitate rapidly formed as soon as the solution became neutral. This was collected, washed well with water and dried at 50° to a yellow powder, m.p. ca. 130° (dec.) (7.0 g., 90%). Crystallization from ether gave small yellow needles, m.p. 148° dec., of the 4-phenylhydrazone of cyclopentene-3, 4,5-trione, while sublimation yielded orange and yellow feathery crystals, m.p. 148° dec., with identical infrared spectrum; principal infrared bands (CCl₄) at: 1673, 1532, 1495, 1484, 1283, 1202, 1168, 1151, 1052, 1020 and 852 cm.⁻¹; λ_{max} (CCl₄): 378 mμ (4.23); (10% aq. EtOH): 378, 223 mμ (4.55, 4.36); (10%, 0.1 N HCl): 380, 224 mμ (4.53, 4.45); (10%, 0.1 N NaOH): 358, 272 mμ (4.47, 4.33).

Anal. Calcd. for C₁₁H₈O₂N₂: C, 65.98; H, 4.03; N, 13.99. Found: C, 65.94; H, 4.11; N, 14.10.

Cold solutions of the phenylhydrazone in ethanol slowly darken, rapidly in the presence of sodium hydroxide, and evaporation yields a dark brown intractable product. Solutions in carbon tetrachloride gave a similar material after a short period under reflux.

Reaction of the Dione with Diazotized p-Nitroaniline.—The dione (2.0 g., 0.02 mole) was treated as described above with p-nitroaniline (2.7 g., 0.02 mole) diazotized in aqueous sulfuric acid to yield a yellow product (4.9 g., 96%). Crystallization from acetone gave long, golden-yellow needles, m.p. 230° dec., of the 4-p-nitrophenylhydrazone of cyclopentene-3,4,5-trione; principal infrared bands (CHCl₃) at: 1681, 1610, 1603, 1550, 1515, 1342, 1143, 1109. and 1020 cm.⁻¹; λ_{max} (CCl₄): 381 mμ (4.20); (95% aq. EtOH): 376, 240 mμ (4.32, 3.98); (95% + aq. NaOH): 262 mμ (4.18), with very strong absorption at 400–420 mμ.

Anal. Calcd. for C₁₁H₇O₄N₃: C, 53.87; H, 2.88; N, 17.13. Found: C, 53.89; H, 2.98; N, 17.15.

The p-nitrophenylhydrazone behaves like the phenylhydrazone above in aqueous ethanolic and sodium hydroxide solutions, but seems to be stable indefinitely in carbon tetrachloride solution.

AMES, IOWA

The Condensation of Aromatic Nitro Compounds with Arylacetonitriles.[1] I. Nitrobenzene

BY R. B. DAVIS, L. C. PIZZINI AND J. D. BENIGNI

Nitrobenzene condenses with arylacetonitriles to produce a new series of compounds, substituted methylenequinone oximes. Proof of structures is offered. A mechanism for the condensation is proposed.

When benzyl cyanide and nitrobenzene are added to a warm solution of methanolic potassium hydroxide, the reaction mixture turns deep-red and a deep-red solid soon precipitates. The solid is soluble in water, and, on acidification of the solution with acetic acid, a yellow-orange solid precipitates in 77% yield. The product has been shown to be 4-(phenylcyanomethylene)-cyclohexa-2,5-diene-1-one oxime (I).

No evidence was obtained for the tautomeric structure II, phenyl-p-nitrosophenylacetonitrile. Likewise, attempts to isolate phenyl-p-hydroxylaminophenylacetonitrile (III) and phenyl-p-nitrophenylacetonitrile (IV) were unsuccessful. Nere-

(1) Research project supported in part by National Science Foundation grant. NSF-G10030.
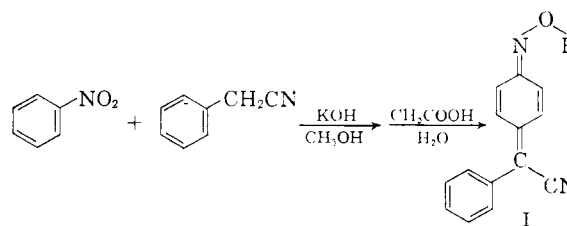
sheimer and Ruppel[2,3] have reported that the reaction of benzyl cyanide and nitrobenzene in pyridine containing finely divided potassium hydroxide gives a mixture of III and IV.

(2) H. Neresheimer and W. Ruppel, German Patent 603,622 (1934).

(3) H. Neresheimer and W. Ruppel, U. S. Patent 2,080,057 (1937).