wave length variations largely in accord with the well known chromophoric properties of their substituents. In the benzaldehyde section of the chart the solid segment at longer wave lengths is composed almost entirely of *o,p*-alkoxy or hydroxy derivatives. The *p*-dialkylamino derivatives absorb well above 400 mμ and do not appear on the chart. The number of aromatic aldehydes of heterocyclic or higher ring systems was too small to justify entry in the table.

7. Acetophenones (or higher homologs) lacking *o*-alkyl substituents or α-substituents resemble the benzaldehydes. (End compounds on the chart are the *p*-nitro and *p*-amino derivatives respectively at left and right.) Apparently *o*-substituents or two α-substituents exert a considerable steric hindrance. The problem is complicated by the fact that a number of α-substituted acetophenones have two isomeric 2,4-dinitrophenylhydrazones absorbing about 20 mμ apart. For a detailed discussion see papers by Ramirez.[5]

8. Tetralones and indanones are logically related to the acetophenones in spectra.

9. Bis-2,4-dinitrophenylhydrazones generally absorb at about the expected wave length for the corresponding mono compounds but with approximately doubled absorbancy. Notable exceptions are the vicinal dicarbonyl compounds, where the 2,4-dinitrophenylhydrazone groups are conjugated with each other, and the maxima included usually a band near 400 and also one around 430 mμ.

Acknowledgment. This work was partially supported by Grant CY-5607 from the National Cancer Institute of the Public Health Service. The author is grateful to Mr. Dudley Robertson for assistance in processing the data.

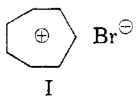
Chemistry Department
University of Louisville
Louisville 8, Ky.

Preparation of Tropilidene Derivatives from Tropylium Bromide

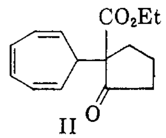
Nedra W. Jordan and I. W. Elliott[1]

Received August 16, 1961

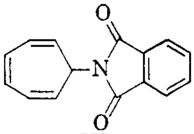
Tropylium bromide (1) has been shown to replace protons on reactive methylene, hydroxyl, amino and amido groups.[2–4] We report here an extension of these reactions in which tropylium bromide is allowed to react with 2-carbethoxycyclopentanone, potassium phthalimide, and 1,3-indandione to afford respectively II, III, and IV. The structures of the products are supported by analyses and infrared spectra. The latter is useful to show the presence of the intact cycloheptatriene ring.[3]



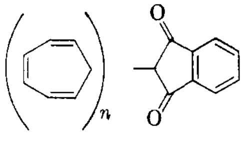
I



II



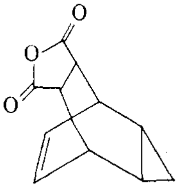
III



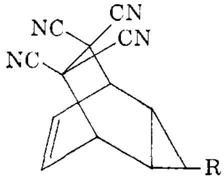
IVa. $n = 1$
b. $n = 2$

The substituted indandiones (IV) were prepared as potential blood anticoagulant drugs.[5] Both 2-tropyl-1,3-indandione (IVa) and 2,2-ditropyl-1,3-indandione (IVb) were isolated, depending on the method of preparation and purification. Compound IVa in dichloromethane solution undergoes a color change from yellow to red on the addition of base, but IVb does not. This change can be ascribed to an increase in the enol content in IVa.[6]

In 1939 Kohler[7] prepared an adduct of tropilidene with maleic anhydride in refluxing xylene. The structure of this compound was resolved in 1953 by Alder and Jacobs as *endo-cis*-3,6-*endo*-cyclopropyl-1,2,5,6-tetrahydrophthalic anhydride (V).[8] A reaction between tropilidene and maleic anhydride at room temperature in ether afforded the same adduct. The yield of the adduct formed under the milder reaction conditions was about half that from refluxing xylene, but no attempts were made to determine optimum conditions for the reaction in ether or to obtain quantitative recovery of the products. In an extension of the Diels-Alder reactions of cycloheptatriene, new adducts (VI) have been synthesized from the dienophile tetracyanoethylene with tropilidene and tropylacetylacetone, and the structures of these products are assigned by analogy with the adduct from maleic anhydride (V) and from similar infrared spectra.



V



VIa. R = H
b. R = -CH(COCH$_3$)$_2$

Weiss and Lalande have discussed the spectra of a series of maleic anhydride adducts with tropilidene derivatives, but they did not explicitly

---

[1] To whom correspondence concerning this note should be addressed.

[2] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 353 (1957).

[3] K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

[4] M. E. Volpin, I. S. Akrem, and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1501 (1957); *Chem. Abstr.*, **52**, 7175c (1958).

[5] See S. L. Shapiro, K. Geiger, and L. Freedman, *J. Org. Chem.*, **25**, 1860 (1960) for a discussion and references on these compounds.

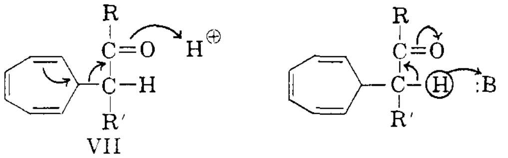
[6] *Cf.* A. Schönberg and F. Singer, *Chem. Ber.*, **94**, 241 (1961); A. Schönberg and G. Schutz, *Chem. Ber.*, **94**, 667 (1961).

[7] W. Kohler, M. Tishler, H. Potter, and H. T. Thomsen, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

[8] K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

identify bands for the cyclopropyl ring.[9] The regions 3.2–3.5, 9.5–10.0 and 11.6 μ have variously been used to identify the cyclopropane ring from infrared spectra.[10] Slabey studied the infrared spectra of thirty-four cyclopropane derivatives and concluded that the 9.5–10.0 μ region was the most suitable for determining the presence of the cyclopropyl ring.[11] Aside from the characteristic bands for the anhydride, cyano and carbonyl groups in V and VI a–b, these adducts each show medium intensity absorption in the regions 9.8–10.0 and 11.6 μ. No comparable bands appear in the spectra of the starting tropilidene compound used in the Diels-Alder reactions. Moreover, an examination of the spectra of the adducts (V and VI) reveals that they do not exhibit a band *ca.* 14.2 μ that appears for compounds with the cycloheptatriene system.

Tropylacetylacetone (VII, R = CH_3, R = $COCH_3$) was prepared by Conrow and shown to exist predominately in the diketo form.[3] In general substitution on the 3-position of acetylacetone shifts the tautomeric equilibrium in favor of the keto isomer.[12] Conrow has suggested that in the case of tropylacetylacetone enolization probably cannot occur without loss of the tropylium ion. This is clearly illustrated in the acid-catalyzed fragmentation of tropylacetylacetone from which tropylium perchlorate can be isolated. In contrast to the mechanism for fragmentation, base-catalyzed enolization should preferentially involve loss of the proton.



VII

To test this possibility, we have attempted unsuccessfully to prepare a copper chelate of tropylacetylacetone under the usual conditions employed for acetylacetone. Furthermore, tropylacetylacetone should undergo the typical condensations of a β-diketone with urea, thiourea, and benzamidine to yield the corresponding 5-cycloheptatrienylpyrimidines. Roberts, however, has pointed out that few α-substituted β-diketones have been employed in pyrimidine condensations with amidines and reports an experiment in which methylacetylacetone is shown to form 2,4,5,6-tetramethylpyrimidine in very low yield.[13] In none of the attempted condensations using tropylacetylacetone has an effective pyrimidine synthesis been demonstrated under a variety of experimental conditions. In practically every case a good recovery of the diketone was obtained.

EXPERIMENTAL[14]

Tropylium bromide. Cycloheptatriene was converted to tropylium bromide by the method of Doering and Knox.[2] The crude tropylium bromide was stored under ether at 0°, and prior to use the solid was dissolved in water, treated with decolorizing charcoal, and filtered to give a clear yellow solution of tropylium bromide.

2-Tropyl-2-carbethoxycyclopentanone (II). An aqueous solution containing approximately 2 g. of tropylium bromide was mixed with 2 ml. of 2-carbethoxycyclopentanone and 0.1 ml. of pyridine. An oil separated, and the aqueous layer was decanted. The oil was dissolved in hot ethanol and solidified on cooling and scratching. The product was recrystallized from aqueous ethanol as colorless crystals, wt. 1.6 g., m.p. 50–51°; λ_{max}^{Nujol} 5.72, 5.83, 8.05, 8.96, 13.38, 13.65, and 14.14 μ.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.85; H, 6.98.

2-Tropyl-1,3-indandione (IVa). A solution of 1.5 g. of 1,3-indandione in ethanol was treated in small portions with an aqueous solution containing 1.9 g. of tropylium perchlorate.[15] After every addition of tropylium salt, 1–2 drops of pyridine was added to retain a purple color, and the solution was well mixed. The solid product slowly separated and was kept overnight before collecting it as a yellow-green solid, m.p. 131–134°, wt. 1.87 g. The crude solid was recrystallized from acetic acid or preferably from dichloromethane-ethanol solution as bright yellow crystals, m.p. 193–194°; λ_{max}^{EtOH} 247 (log ϵ 4.24); 328 mμ (log ϵ 3.89); λ_{min} 296 mμ (log 3.69); λ_{max}^{KBr} 5.83, 5.93 μ.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12; M.W. 236. Found: C, 81.58; H, 4.92; M.W. 259.

The bis-2,4-dinitrophenylhydrazone of IVa was prepared, m.p. 253–254° (dec).

Anal. Calcd. for $C_{28}H_{20}N_8O_8$: N, 18.6. Found: N, 18.4.

2,2-Ditropyl-1,3-indandione (IVb). An aqueous solution from 1.7 g. of crude tropylium bromide was treated with a suspension of 1.0 g. of 1,3-indandione in aqueous alcohol. The mixture became turbid, and 0.5 ml. of pyridine was added with stirring. A gummy semisolid first separated, but it gave a granular solid when stirred 1 hr. and kept at 0° overnight. The yellow solid, wt. 1.7 g., 110–120°, was collected; the crude product dissolved with difficulty in ethanol to afford a deep red solution that slowly deposited crystalline product. Several recrystallizations from ethanol-acetonitrile finally gave 0.3 g. of a constant melting pale yellow solid, m.p. 173–174°; λ_{max}^{KBr} 5.78 (medium), 5.87 (strong), 7.98, 12.61, 13.04, 13.52, and 14.20 μ.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.88; H, 5.46.

N-Tropylphthalimide (V). To a suspension of 0.5 g. of potassium phthalimide in water was added a charcoal-treated solution of 0.4 g. of tropylium bromide. Immediately a milky precipitate formed. The mixture was stirred well and allowed to stand overnight. The solid, wt. 0.6 g., m.p. 155–158°, was recrystallized from ethanol as almost colorless needles, m.p. 170–171°; λ_{max}^{KBr} 5.67 (medium), 5.83 (strong), 9.02, 11.52, 12.48, 13.17, 13.59, 13.90, and 14.2 μ.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 76.22; H, 4.66; N, 6.13.

Diels-Alder reaction of cycloheptatriene with maleic an-

---

[9] K. Weiss and M. L. Lalande, *J. Am. Chem. Soc.*, **82**, 3117 (1960).

[10] *Cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, N. Y., 2nd Ed., 1958, p. 29.

[11] V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3604 (1954).

[12] *Cf.* G. Hammond, "Steric Effects in Organic Chemistry," M. S. Newman, ed., J. Wiley and Sons, Inc., New York, 1956, p. 442.

[13] J. C. Roberts, *J. Chem. Soc.*, 3065 (1952).

[14] The melting points are uncorrected. Analyses are by Schwarzkopf Microanalytical Laboratory. We thank Shell Chemical Corp. for a generous gift of cycloheptatriene.

[15] D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk S.S.S.R.*, **113**, 339 (1957); *Chem. Abstr.*, **51**, 14572 (1957); K. Conrow, *J. Am. Chem. Soc.*, **83**, 2346 (1961).

hydride. A solution of 2.0 g. of cyclopheptatriene and 2.1 g. of maleic anhydride in 15 ml. of anhydrous ether was allowed to stand at room temperature for 24 hr. The solvent was partially evaporated to one-third the original volume, and 1.7 g. of solid, m.p. 95–98°, was collected. Recrystallization of the product from carbon tetrachloride afforded colorless crystals, m.p. 102–103°, that proved on the basis of m.m.p. and infrared spectra to be identical with the adduct prepared in refluxing xylene.[5,7]

Diels-Alder reaction of cycloheptatriene with tetracyanoethylene. A solution of 0.1 g. of tetracyanoethylene in 12 ml. of tetrahydrofuran was mixed with 1 ml. of cycloheptatriene. A deep red color developed on mixing and faded on standing. After 12 hr. the product was precipitated by carbon tetrachloride as 0.22 g. of pale yellow crystals, m.p. 157–160° (dec.). Recrystallization from ethanol afforded colorless crystals, m.p. 160–161° (dec.); $\lambda_{\max}^{\text{Nujol}}$ 4.49, 9.82, 11.61, and 13.55 μ.

Anal. Calcd. for $C_{13}H_8N_4$: C, 70.88; H, 3.66; N, 25.46. Found: C, 70.90; H, 3.73; N, 24.99.

Diels-Alder reaction of tropylacetylacetone with tetracyanoethylene. To a solution of 0.3 g. of tetracyanoethylene in 10 ml. of tetrahydrofuran was added 0.3 g. of tropylacetylacetone in 10 ml. of tetrahydrofuran. The solution was allowed to stand overnight, and 0.42 g. of colorless crystals m.p. 174–175° (dec.) was obtained. For analysis the sample was recrystallized from acetonitrile. The infrared spectrum shows bands at 4.50, 5.79, 9.80, 11.60, and 13.45 μ.

Anal. Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.90; H, 4.44; N, 17.61. Found: C, 68.50; H, 4.78; N, 17.93.

Attempted Reactions of Tropylacetylacetone. (a) *Chelation with copper*(II) *salts.* When cupric acid and tropylacetylacetone were heated in dimethylformanide or in a mixture of acetic acid sodium acetate no evidence of chelate formation was obtained. An attempted reaction by the method of Garg[16] failed to afford a chelate of the substituted β-diketone.

(*b*) *Attempted condensation of tropylacetylacetone with benzamidine.* Tropylacetylacetone (0.1 g.) and 0.1 g. of benzamidine were dissolved in 15 ml. of ethanol and warmed for 5 min. Five milliliters of acetic acid was added, and the solution was boiled 10 min. and allowed to stand overnight. The solution was filtered, and the precipitate (0.9 g.) colsected and air dried, m.p. 123–125°. Recrystallization from ethanol afforded white crystals, m.p. 124–125°. Infrared analysis and a mixed m.p. showed the product to be identical with tropylacetylacetone. Subsequent trials, using basic catalysis, were similarly unsuccessful.

(*c*) *Reaction of tropylacetylacetone with urea.* Three grams of tropylacetylacetone and 1.5 g. of urea in ethanol using sodium hydroxide as catalyst were refluxed for 5 hr. On cooling a small amount of colorless solid, m.p. 300°, was obtained. The filtrate was concentrated, and crystals were obtained that slowly melted when they were collected on the funnel. The oily residue was redissolved in ethanol and further unsuccessful attempts to obtain crystals were made.

In one run urea (0.1 g.) and tropylacetylacetone (0.1 g.) were dissolved in pyridine and heated for 0.5 hr.; only unchanged starting materials were obtained by fractional crystallization.

(*d*) *Reaction of tropylacetylacetone with thiourea.* A solution of 1.0 g. of thiourea, 0.8 g. of tropylacetylacetone and 0.1 g. of sodium hydroxide in ethanol were heated intermittently, slowly driving off the alcohol. The total heating time was about 4 hr., and the concentrated solution on cooling deposited a small portion of inorganic salts. The second crop of crystals proved to be unchanged thiourea (0.9 g.) by m.p. and infrared identification.

DEPARTMENT OF CHEMISTRY
FISK UNIVERSITY
NASHVILLE, TENN.

---

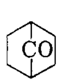
[16] H. G. Garg, *J. Org. Chem.*, **26**, 948 (1961).

The Pyrolysis of Barium 1,4-Cyclohexanedicarboxylate

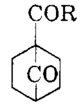
C. F. H. ALLEN,[1a] G. A. REYNOLDS, S. K. WEBSTER, AND J. L. R. WILLIAMS

Received July 26, 1961

Sixty years ago, Zelinsky[1b] reported that, upon the distillation of the barium salt of 1,4-cyclohexanedicarboxylic acid, a fraction of the distillate gave a semicarbazone which melted at 209–210°; the carbonyl compound was not regenerated. However, the assumption was made that the semicarbazone was derived from the carbonyl bridged compound I. It seemed advisable to repeat this work and to identify the substance containing the carbonyl group.



I



IIa. R = OH
b. R = OCH_3
c. R = Cl

Benzaldehyde and *o*-tolualdehyde, rather than 7-oxo-1,4-methanocyclohexane (I) as claimed by Zelinsky, are the carbonyl compounds obtained by the dry distillation of the barium salt of 1,4-cyclohexanedicarboxylic acid. By the use of infrared spectra, the *absence* of a band at 5.64 mμ, characteristic for a carbonyl group across a six-membered ring, was noted.[2] However, there was a strong band for an aromatic aldehyde carbonyl. The crude oil obtained from the dry distillation was fractionated *in vacuo*, and a portion of the fraction giving a dinitrophenylhydrazone was converted to this derivative and submitted to paper chromatography. Two of the 2,4-dinitrophenylhydrazones were identified as those of benzaldehyde and *o*-tolualdehyde, and there were small amounts of three others, apparently derived from products of ring cleavage.

It is highly probable that the dicarboxylic acid (as barium salt) first loses formic acid to give a cyclohexenemonocarboxylate, the usual aldehyde synthesis from a carboxylate and a formate, thus accounting for the aldehyde. The time of dehydrogenation is unknown, but the occurrence of methane suggests that a greater part of the salt is decarboxylated and reduced. A slight reduction of carboxyl to methyl is indicated by the presence of the tolualdehyde; such a behavior has been noted in a zinc dust reduction.[3]

In the mass spectrum, a band of mass 126 cor-

---

(1)(a) Present address: Rochester Institute of Technology, Rochester, N. Y. (b) N. D. Zelinsky, *Ber.*, **34**, 3798 (1901).

(2) C. F. H. Allen, T. Davis, D. W. Stewart, and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

(3) Weidel, *Monatsh.*, **3**, 75 (1882).