**Bis(2-(3-pyridyl)-2,3-dihydrobenz[*f*]indene-1,3-dione) Hydrochloride (IV).**—By application of the sequence of reactions described for III to naphthalene-2,3-dicarboxylic acid, the complex hydrochloride IV was obtained.

**2-(4-Pyridyl)-1,3-indandione (V).**—Refluxing a combination of 13.4 g (0.10 mole) of phthalide, 10.79 g (0.10 mole) of 4-pyridinecarboxaldehyde, 48 ml of dry ethyl propionate, and 16.29 g (0.30 mole) of sodium methoxide dissolved in 100 ml of methanol produced a deep red solution after 2 hr. Evaporation of all solvent, partitioning between ether-water, and strong acidification of the basic aqueous layer with 6 *N* hydrochloric acid produced an orange solid. Recrystallization from a large volume of ethanol yielded the zwitterionic V, mp 325° dec.[12]

*Anal.* Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 74.98; H, 4.24; N, 6.11.

A silver nitrate test on this solid in ethanolic solution did not precipitate silver chloride. Infrared absorptions at 3–5 ($NH^+$) and 6.0 $\mu$ (C=O). An ultraviolet spectrum in 0.1 *N* sodium hydroxide exhibited $\lambda_{max}$ 243 ($\epsilon$ 12,800), 296 (25,200), 332 (19,700), and 346 m$\mu$ (20,500); in methanol 232 ($\epsilon$ 32,400), 295 (8200), and 380 m$\mu$ (47,000). An nmr spectrum (DMSO-$d_6$) showed $\tau$ 2.44 (s, 4-H), 1.06 ($J$ = 3.2 cps) (d, 2-H, the 2- and 6-pyridine protons), and 1.74 ($J$ = 3.2 cps) (d, 2-H; the 3- and 5-pyridine protons). In DMSO-$d_6$ containing 2 drops of 40% sodium hydroxide, V showed $\tau$ 2.48 (s, 4-H), 1.18 ($J$ = 3.2 cps) (d, 2-H), and 1.68 ($J$ = 3.2 cps) (d, 2-H). Titration of V [dioxane-$H_2O$ (2:1)] gave neut equiv 230 (calcd neut equiv 224) and a $pH_{1/2}$ of 8.80.

A **hydrochloric acid salt** (**Va**) of V was prepared in a large volume of hot methanolic hydrochloric acid. Cooling produced an orange solid, mp 312° dec.

*Anal.* Calcd for $C_{14}H_9NO_2 \cdot HCl$: C, 64.74; H, 3.88; Cl, 13.70; N, 5.40. Found: C, 64.43; H, 3.87; Cl, 13.54; N, 5.38.

Titration of Va [dioxane-$H_2O$ (2:1)] indicated a dibasic acid of neut equiv 265 and 131 (calcd neut equiv 260 and 130) with corresponding $pH_{1/2}$ of 2.6 and 8.7. The ultraviolet spectrum was $\lambda_{max}^{MeOH}$ 232 ($\epsilon$ 33,200), 295 (4500), 305 (7500), and 379 m$\mu$ (52,600). The infrared spectrum was 3.25 (OH), 4–5 ($NH^+$), and 5.9 $\mu$ (C=O), indicating an enol form for this monohydrochloride.

**2-(2-Pyridyl)-1,3-indandione (VI).**—Conditions for the preparation of VI were identical with those applied to I except that pyridine 2-carboxaldehyde was used. Acidification with aqueous hydrochloric acid precipitated 17.3 g (35%) of VI, mp 292° dec (sintered at 285°) (lit.[13,3a] 260°; made by treating 2-picoline with phthalic anhydride).

*Anal.* Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.51; H, 3.96; N, 6.23.

A silver nitrate test on VI failed to precipitate silver chloride and VI showed only slight solubility in dilute sodium bicarbonate while dissolving to a red solution in 10% sodium hydroxide. Infrared absorptions of very broad bands were between 3 and 5 $\mu$ (hydrogen bonded OH); a single carbonyl peak was at 6.01 $\mu$. The ultraviolet spectrum in 0.1 *N* sodium hydroxide was $\lambda_{max}$ 250 (sh) ($\epsilon$ 13,900), 278 (18,700), 332 (12,600), and 340 m$\mu$ (sh) (12,250). In methanol solution the results were 230 ($\epsilon$ 23,800), 288 (24,600), 308 (9700), 322 (8350), and 382 m$\mu$ (24,200). An nmr spectrum could not be obtained on the highly insoluble VI.

**Registry No.**—I, 10478-89-4; Ia, 10478-90-7; Ib, 10478-91-8; Ic, 10478-92-9; Id, 10478-93-0; Ie, 10478-94-1; II, 10478-95-2; III, 10478-96-3; IIIa, 10478-97-4; IV, 10478-98-5; V, 10478-99-6; Va, 10479-00-2; VI, 641-63-4; 4-trifluoromethylphthalic acid, 835-58-5.

**Acknowledgment.**—The author is grateful to Mr. Ronald Seidell and Mr. Nelson Treadway, Jr., for assistance in the synthetic work.

# An Improved Synthesis of Spiro[2.5]octa-4,7-dien-6-ones

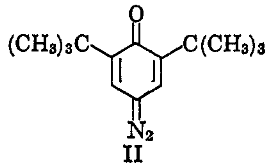
G. F. Koser and W. H. Pirkle

*Noyes Chemical Laboratory, University of Illinois,*
*Urbana, Illinois 61801*

*Received January 17, 1967*

While 4,4-disubstituted cyclohexa-2,5-dienones have been studied extensively, the chemistry of the spiro-[2.5]octa-4,7-dien-6-ones (I) has only recently attracted interest.[1,2] Presumably, their inaccessibility has deterred their study. Only a few examples of these spirodienones are known, there being but two previously reported synthetic approaches. The addition of diazoalkanes to methylenecyclohexadienones with subsequent loss of nitrogen has been little explored.[3,4] While studying neighboring-group participation, Winstein and Baird prepared spiro[2.5]octa-4,7-dien-6-one (I) from 2-*p*-hydroxyphenylethyl bromide in 2% yield.

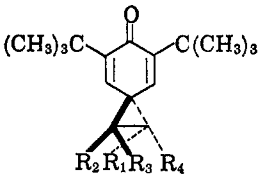
I



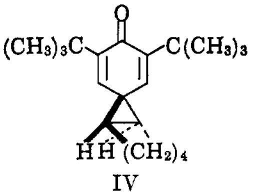
II

These authors report I to be extremely labile toward nucleophiles or traces of acid or base. This paper reports a synthetic approach to spiro[2.5]octa-4,7-dien-6-ones which appears to be superior to those previously reported for it affords a variety of these reactive spirodienones in good yield from readily available precursors.

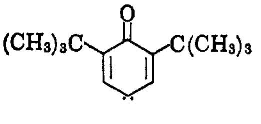
Photolysis of 3,5-di-*t*-butylbenzene 1,4-diazooxide (II) in 2,3-dimethyl-2-butene leads to the formation of 1,1,2,2-tetramethyl-5,7-di-*t*-butylspiro[2.5]octa-4,7-dien-6-one (IIIa) in 80% yield. Use of cyclohexene as a solvent leads to dienone IV in 72% yield. Irradiation of II in neat *cis*- or *trans*-2-butene yields the corresponding *cis*- (IIIb) or *trans*-1,2-dimethylspiro-octadienone (IIIc) with 95 and 97+% stereoselec-



IIIa, $R_1 = R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = H; R_3 = R_4 = CH_3$
c, $R_1 = R_3 = H; R_2 = R_4 = CH_3$
d, $R_1 = R_2 = H; R_3 = R_4 = Cl$



IV



V

---

[12] S. P. Dutta, A. K. Acharyya, and U. P. Basu [*J. Indian Chem. Soc.*, **43**, 549 (1966)] have recently reported mp 319° for this compound ("4-pyrophthalone") prepared from 4-picoline and phthalic anhydride. These authors appear not to have considered a zwitterionic structure for this compound even when the compound failed to form a phenylhydrazone or oxime derivative.

[13] E. Jacobsen and C. L. Reimer, *Ber.*, **16**, 2602 (1883).

[1] (a) S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756 (1957); (b) R. Baird and S. Winstein, *ibid.*, **79**, 4238 (1957); (c) R. Baird and S. Winstein, *ibid.*, **85**, 567 (1963).

[2] (a) D. I. Schuster and C. J. Polowczyk, *ibid.*, **88**, 1722 (1966); (b) D. I. Schuster and I. S. Krull, *ibid.*, **88**, 3456 (1966).

[3] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

[4] D. H. R. Barton and J. B. Hendrickson, *ibid.*, 1028 (1956).

TABLE I

SPIRO[2.5]OCTA-4,7-DIEN-6-ONES

| Compd | Structure |  |  |  | % purity of crude product[a] | % yield | Mp,[b] °C | Carbon, %[c,d] |  | Hydrogen, %[c,d] |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | $R_1$ | $R_2$ | $R_3$ | $R_4$ |  |  |  | Calcd | Found | Calcd | Found |
| IIIa | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | 83 | 79 | 169–170 | 83.27 | 82.97 | 11.19 | 10.93 |
| IIIb | H | H | $CH_3$ | $CH_3$ | 84 | 70 | 128.5–130 | 83.01 | 83.19 | 10.84 | 10.80 |
| IIIc | H | $CH_3$ | H | $CH_3$ | 95 | 95 | 73–74 | 83.01 | 82.97 | 10.84 | 10.94 |
| IIId | H | H | Cl | Cl | 45 | 45 | 109.5–110.5 | 63.46 | 63.68 | 7.36 | 7.34 |
| IV | H | H | $C_4H_8$ |  | 74 | 72 | 129–131 | 83.85 | 83.70 | 10.55 | 10.52 |

[a] Purity was determined by nmr using durene as an internal standard. [b] Reichert block, uncorrected. [c] Analyses were performed by Mr. J. Nemeth and associates of the University of Illinois. [d] The molecular weights of all samples were determined mass spectrometrically by J. Wrona and were found to corroborate the proposed structures. An Atlas CH-4 spectrometer was used.

TABLE II

SPECTRAL PROPERTIES OF SPIRO[2.5]OCTA-4,7-DIEN-6-ONES

| Compd | Carbonyl, $\nu_{max}$ ($cm^{-1}$)[a] | $\lambda_{max}$, $m\mu$[c] | $\epsilon$ | Proton magnetic resonance, $\tau$[d,e] |  |  |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Vinyl | *t*-Butyl | Methine | Methyl |
| IIIa | 1612 and 1632 | 289 | 19,700 | 3.42 (s) | 8.74 (s) | ... | 8.60 (s) |
| IIIb | 1612 and 1637 | 281 | 17,600 | 3.67 (d) and 4.18 (d) | 8.82 (s) and 8.85 (s) |  | 8.76 (d) |
| IIIc | 1617 and 1639 | 281 | 18,900 | 3.78 (s) | 8.76 (s) |  | 8.66 (d) |
| IIId | 1626[b] and 1640 | 271 | 16,700 | 3.35 (d) and 4.18 (d) | 8.72 (s) and 8.76 (s) | 6.18 (s) | ... |
| IV | 1617 and 1640 | 285 | 17,400 | 3.20 (d) and 4.01 (d) | 8.72 (s) and 8.75 (s) |  | ... |

[a] In carbon tetrachloride. Spectra were determined by means of a Perkin-Elmer 521 spectrophotometer. [b] In chloroform. [c] In cyclohexane using a Perkin-Elmer 202 spectrophotometer. [d] Doublet (d), singlet (s). [e] Spectra were obtained on *ca.* 5% solutions in carbon tetrachloride except for IIId and IV which were examined in deuteriochloroform. Varian A-60, A-60A, and A-56/60A spectrometers were used.

tivity. The two stereoisomers are readily distinguished by nmr spectroscopy since both *t*-butyl groups and both vinyl protons are nonequivalent in the *cis* isomer but equivalent in the *trans* isomer. The high yields, stereoselectivity, and convenience of this procedure make it an attractive method for the preparation of spiro[2.5]octa-4,7-dien-6-ones. Table I lists spirodienones which have been prepared in this fashion; Table II presents selected spectroscopic data for these compounds.

Diazooxide II is readily obtained by diazotization of the stannous chloride adduct of 2,6-di-*t*-butyl-4-aminophenol hydrochloride which is in turn prepared from the corresponding nitrophenol.[5] Oxygen-free solutions of II ($\lambda_{max}$ 510 m$\mu$) in neat olefin were irradiated through a potassium chromate–dichromate solution to absorb light of wavelength less than 480 m$\mu$, reaction progress being monitored by nitrogen evolution, by disappearance of the strong 2170-$cm^{-1}$ diazo band, or by disappearance of the orange diazooxide color. The crude spirooctadienones were isolated by evaporation of the excess olefin and recrystallized from cold pentane. Owing to the mildness of the reaction conditions and to the use of a filter which prevents direct excitation of the photolabile spirooctadienones,[2] the crude products are of 75–95% purity.

Although spirooctadienone formation may result from addition of carbene V to the olefinic substrate, the intermediacy of an unstable pyrazoline may not yet be excluded. Carbene intermediates have been postulated to explain the formation of biphenyl phenols when various benzene-1,4-diazooxides are decomposed in aromatic solvents.[6] The results of a study of the mechanism of spirooctadienone formation will be subsequently reported.

## Experimental Section

**Stannous Chloride Adduct of 2,6-Di-*t*-butyl-4-Aminophenol Hydrochloride.**—A 1-l., three-necked, round-bottom flask, fitted with a magnetic stirring bar and an addition funnel, was charged with 15.0 g (0.060 mole) of 2,6-di-*t*-butyl-4-nitrophenol, 300 ml of water, 150 ml of tetrahydrofuran, and 30 g of granulated tin. While maintaining a nitrogen atmosphere, 75 ml of concentrated hydrochloric acid was added dropwise to the stirred suspension over a 2-hr period.

When the addition was complete, an equal volume of methylene chloride was added and, after thorough mixing, the lower organic layer was collected and concentrated to dryness at reduced pressure. Trituration of the brown solid residue with benzene afforded 25.0 g (93%) of the colorless tin complex which decomposes at *ca.* 200° without melting.

*Anal.* Calcd for $C_{14}H_{24}Cl_3NSn$: C, 37.58; H, 5.41; Cl, 23.78; N, 3.13. Found: C, 37.56; H, 5.41; Cl, 23.28; N, 3.07.

Treatment of a saturated mercuric chloride solution with a solution of the complex salt in 6 *M* hydrochloric acid precipitates mercurous chloride, thus establishing that the tin in the complex is divalent. The aminophenol itself fails to reduce mercuric ion under these conditions.

**3,5-Di-*t*-butylbenzene 1,4-Diazooxide.**—A 1-l., three-necked, round-bottom flask, fitted with a stirring bar, addition funnel, and nitrogen inlet was charged with a suspension of 18.4 g (0.044 mole) of 2,6-di-*t*-butyl-4-aminophenol–stannous chloride hydrochloride in 500 ml of *ca.* 1 *M* hydrochloric acid. The reaction mixture was then cooled to 0° and continuously blanketed with nitrogen while 225 ml of cold 2–4% aqueous sodium nitrite was added dropwise over a 2-hr period. Care must be taken to protect the subsequently formed reddish orange water-insoluble diazooxide from light during its isolation and purification. After being collected by suction filtration, the crude product (8.0 g) may be stored in the cold without decomposition. Purification may be effected by chromatography with methylene chloride upon Brinkmann silica gel, the third colored band to be eluted being **3,5-di-*t*-butylbenzene 1,4-diazooxide**. The yield of purified material, based upon the tin complex, is *ca.* 55%. The purified diazooxide, which melts with decomposition at 98–118°, exhibits strong carbonyl (1580 $cm^{-1}$) and diazo (2070 $cm^{-1}$) infrared absorptions (chloroform solution) and ultraviolet and visible absorption bands (cyclohexane solution) at 270 m$\mu$ ($\epsilon$ 4120), 353 (26,300), and 510 (33). The 60-MHz nmr spectrum in deuteriochloroform consists of two singlets (1:9 areas) at $\tau$ 2.84 and 8.66.

*Anal.* Calcd for $C_{14}H_{20}N_2O$: C, 72.37; H, 8.68; N, 12.06. Found: C, 72.39; H, 8.71; N, 11.99.

---

(5) We wish to thank the Ethyl Corp. for a generous gift of 2,6-di-*t*-butyl-4-nitrophenol.

(6) C.-H. Wang, *Proc. Chem. Soc.*, 309 (1961); (b) J. K. Stille, P. Cassidy, and L. Plummer, *J. Am. Chem. Soc.*, **85**, 1318 (1963); (c) M. J. S. Dewar and K. Narayanaswami, *ibid.*, **86**, 2422 (1964), and references cited therein.

**Photolysis of 3,5-Di-*t*-butylbenzene 1,4-Diazooxide in Olefins.**—Two slightly different procedures were followed depending upon whether or not the olefin boiled above 25°. One example of each procedure will be given.

A. **Procedure for Liquid Olefins.**—A cylindrical (29-mm od) Pyrex vessel fitted with a Dry Ice condenser, nitrogen inlet, and drying tube was charged with a solution of 0.419 g (1.80 mmoles) of freshly purified 3,5-di-*t*-butylbenzene 1,4-diazooxide in 42 ml of freshly purified 2,3-dimethylbutene-2. This vessel was immersed in a 49-mm o.d. Pyrex cylinder containing a filter solution (0.002 $M$ potassium chromate–0.006 $M$ potassium dichromate in water) which absorbs wavelengths below 480 m$\mu$. An external cylindrical Pyrex vessel filled with ice and water served to maintain the temperature of the reaction mixture and filter solution between 0 and 10°. While the olefin solution was continuously purged with nitrogen, this concentric array was irradiated with a 275-w, G.E. sun lamp (*ca.* 15 cm from the sample) until the 2070-cm$^{-1}$ diazo band had disappeared (*ca.* 4 hr). When the photolysis was complete, reduced pressure evaporation of the olefin left 0.496 g of crude 1,1,2,2-tetramethyl-5,7-di-*t*-butyl-spiro[2.5]octa-4,7-dien-6-one as a yellow solid which was recrystallized from pentane (−78°) until colorless.

B. **Procedure for Gaseous Olefins.**—A small Teflon-coated stirring bar and 0.500 g (2.15 mmoles) of the purified diazooxide were placed in a 19 × 25 × 615 mm Pyrex combustion tube which was fitted with a Dry Ice condenser, nitrogen inlet, drying tube, and olefin inlet. The combustion tube was partially immersed in a Dry Ice–acetone bath while 50 ml of *cis-* (or *trans-*) 2-butene (99 +% purity) was slowly condensed into the tube. The cold olefinic solution was frozen in liquid nitrogen and degassed by several freeze–pump–thaw cycles, and the tube was sealed while evacuated. The actual irradiation and work-up were carried out as described in part A.

**Registry No.**—II, 955-02-2; IIIa, 10472-75-0; IIIb, 10472-76-1; IIIc, 10472-77-2; IIId, 10472-78-3; IV, 10472-79-4; stannous chloride adduct of 2,6-di-*t*-butyl-4-aminophenol hydrochloride, 13052-54-5.

**Acknowledgment.**—This work was partially supported by an unrestricted research grant from the Rohm and Haas Co.

---

## Conformational Analysis. LV. On the Enol Contents of the Cyclanones and the Alternation of Enol Content with Chain Length in the Alkanones[1,2]

NORMAN L. ALLINGER, LIBBY W. CHOW, AND R. A. FORD

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

*Received November 8, 1966*

In a series of papers,[3] Gero has reported measurements of the enol contents of a number of cyclic and acyclic ketones, and the results, if correct, present quite a challenge in interpretation to the available methods of conformational analysis.[4] Specifically, there are two dramatic features that may be noted. The first of these is the alternation in enol content with chain length well beyond the distance to which such an alternation might be expected. Thus for example, the members of the series of methyl alkyl ketones, as the alkyl group goes from ethyl to *n*-hexyl, are reported to contain enol contents in the following percentages: 0.12, 0.01, 0.11, 0.10, 0.92. The other unusual point is the large enol contents reported for the cycloalkanones, for instance 9.3% in cyclooctanone, and 4.0% in cyclononanone.

Gero's work was done before the availability of some of the modern physical methods, and was based on a modification of the Kurt Meyer titration. Because of the most unexpected nature of the results obtained by Gero, and because of the potential importance of such results in conformational analysis, we considered it desirable to check some of these numbers by a physical method which did not depend upon a chemical reaction, and the attendant uncertainties. We chose nmr spectroscopy as the method and decided to check specifically the enol contents of cyclohexanone, cycloheptanone, and cyclooctanone, which were reported to be 1.18, 0.56, and 9.3%, respectively.[5] Other studies of enol contents of cyclohexanone under various conditions have found only very small amounts of enol ($10^{-2}$–$10^{-6}$%).[6]

A similar determination of the (large) enol content of acetylacetone was reported some years ago by Reeves.[7] We repeated the measurements reported by Reeves on acetyl acetone, and obtained substantially the same results. We next determined the nmr spectra of cyclohexanone, cycloheptanone, and cyclooctanone in methanol under conditions reasonably similar to those used for the chemical determination by Gero.[8] We then repeated the measurements in carbon tetrachloride solvent for cycloheptanone. In no case were we able to detect any presence of a vinyl hydrogen. Even allowing for considerable splitting, it is quite impossible that cyclooctanone could contain such a large proportion of enol, and have the latter remain undetected. For cycloheptanone, it was not immediately obvious that the sample contained less than the stated amount of enol, although none was detected. A sample was therefore prepared which contained 0.00923 g of benzene (for use as an internal concentration standard), and 1.41746 g of cycloheptanone, in a solvent mixture made from 0.192 g of methanol and 0.116 g of water. The stated percentage of enol in cycloheptanone should have yielded a vinyl proton resonance with one-seventh of the area of that given by the benzene in our sample, or a peak height of about 1.5 cm under the condition used, if no allowance is made for splitting. No peak was detectable in the region where vinyl absorbtion was expected, even when this region was scanned very slowly while integrating (the vinyl H of cycloheptanone enol acetate is at $\tau$ 5.0 and that of cycloheptanone enol ether is at 5.36), and it was concluded that no more than 0.2% enol could be present and remain undetected. Similarly, it was estimated that no more than 0.4% enol could be present in chloroform.[9]

---

[1] Paper LIV: N. L. Allinger, J. Allinger, L. W. Chow, and G. L. Wang, *J. Org. Chem.*, **32**, 522 (1967).

[2] This research was supported by Grant GP 1174 from the National Science Foundation.

[3] A. Gero, *J. Org. Chem.*, **26**, 3156 (1961); **19**, 1960 (1954); **19**, 469 (1954).

[4] E. L. Eliel, N. L. Allinger, G. A. Morrison, and S. J. Angyal, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965.

[5] A Varian Associates A-60A nmr spectrometer (signal/noise = 16) was used.

[6] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947); R. P. Bell and P. W. Smith, *J. Chem. Soc.*, 241 (1966); J. E. Dubois and G. Barbier, *Bull. Soc. Chim. France*, 682 (1965).

[7] L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

[8] Gero used 75% methanol as solvent, while 61–78% methanol was used in the present work.

[9] A 0.25% solution of cycloheptanone enol acetate easily showed the expected triplet at $\tau$ 5.0.