Anal. Calcd. for $C_{15}H_{22}O_2NCl$: O, 11.28; N, 4.94; Cl, 12.49. Found: O, 10.95; N, 4.93; Cl, 12.64.

3-Phenyl-4-piperidinobutyric Acid (XXV).—Lactone XXXII (1.0 g.) was dissolved in 95% ethanol (50 ml.) and hydrogenated at room temperature and atmospheric pressure in the presence of 10% palladium-on-charcoal (100 mg). Two moles of hydrogen per mole of XXXII was absorbed. The catalyst was separated by filtration, and the filtrate evaporated to dryness at 40° *in vacuo*. The solid residue (0.9 g. of essentially pure XXV) was recrystallized from ethyl acetate and yielded colorless, extremely water-soluble crystals, m.p. 154–157°.

Anal. Calcd. for $C_{15}H_{21}O_2N$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.70; H, 8.68; N, 5.49.

A hydrochloride was obtained by treating a solution of XXV in anhydrous ethyl acetate with 4 *N* HCl in anhydrous ethyl acetate, and recrystallizing the precipitate from anhydrous alcohol, m.p. 210–214°. Its infrared spectrum in Nujol proved to be identical with the one of compound XXIII. Mixed m.p. of the two hydrochlorides was without depression.

Ethyl 3-Phenyl-4-piperidinobutyrate (XXVII). (a) From XXV.—Acid XXV (0.5 g.) was dissolved in ethanol (10 ml.) and treated with 30 ml. of a 1 *M* ethereal diazoethane solution. The oily residue of the evaporated solution was dissolved in methylene chloride. The infrared spectrum of this solution was identical with the one of compound XXVII prepared as described under (b).

(b) From XXVII.—A solution of 4.50 g. of ethyl β-formyldihydrocinnamoate,[12] 1.89 g. of piperidine and a catalytic amount of *p*-toluenesulfonic acid in 20 ml. of anhydrous benzene was boiled for 2.5 hr. in an open flask. The evaporating benzene was replaced every 10 minutes by anhydrous benzene. The reaction mixture was then evaporated *in vacuo* and yielded 5.6 g. of enamine XXVIII as a yellow oil.

Crude XXVIII (0.5 g.) was dissolved in anhydrous ethyl acetate (25 ml.) and hydrogenated at room temperature and atmospheric pressure in the presence of 10% palladium-on-charcoal (100 mg.); 1 mole of hydrogen per mole of XXVIII was absorbed rapidly. The catalyst was separated by filtration, and the filtrate evaporated *in vacuo*. The infrared spectrum of the oily residue in methylene chloride was identical with the one of compound XXIV prepared as described under (a).

1,1,2-Trifluoro-3-phenyl-4-piperidino-2-cyclobutene (VII).—To a solution of 10.9 g. of 1,1,2-trifluoro-2-chloro-3-phenylcyclobutene (VI) in 30 ml. of anhydrous benzene was added dropwise a solution of 10 ml. of anhydrous piperidine in 20 ml. of anhydrous benzene. The reaction mixture was heated to 50° for 30 minutes. The precipitated piperidine hydrochloride (6.05 g) was then removed by filtration. The filtrate was evaporated at 40° *in vacuo*. The residue (13.0 g. of essentially pure VII) crystallized after standing overnight. It was recrystallized from methanol and yielded colorless VII, m.p. 40–42°.

Anal. Calcd. for $C_{15}H_{16}NF_3$: C, 67.40; H, 6.03; N, 5.24. Found: C, 67.15; H, 5.78; N, 5.27.

1,1-Difluoro-2,4-dipiperidino-3-phenylcyclobutene (IX).—To a solution of 99.0 g. of 1,1-difluoro-2,4-dichloro-3-phenylcyclobutene (VIII) in 270 ml. of anhydrous benzene was added dropwise a solution of 225 ml. of anhydrous piperidine in 225 ml. of anhydrous benzene. The reaction mixture was then kept at 60° for 60 minutes. The precipitated piperidine hydrochloride (97.0 g.) was removed by filtration. The filtrate was evaporated at 45° *in vacuo*, whereby 143 g. of IX was obtained in form of a yellow oil. A sample of this oil was dissolved in anhydrous ethyl acetate, and a solution of HCl in the same solvent added. The colorless monohydrochloride thus obtained was recrystallized from chloroform–ethyl acetate, m.p. 158–160°. During this process piperidine hydrochloride would occasionally crystallize with the hydrochloride IX.

Anal. Calcd. for $C_{20}H_{27}N_2ClF_2$: C, 65.12; H, 7.38; N, 7.59; Cl, 9.61. Found: C, 64.10; H, 7.52; N, 7.65; Cl, 9.91.

4,4-Difluoro-2-phenylcyclobutenone (XII).—Crude hydrochloride IX (3.2 g.) was suspended in 30 ml. of 2 *N* hydrochloric acid and kept at 70° for 45 minutes. The reaction mixture was cooled to room temperature, whereby the separated oil solidified. It was crystallized from chloroform–pentane and yielded 1.1 g. of colorless crystals, m.p. 83–86°, which easily sublime at 0.03 mm. and 40°.

Anal. Calcd. for $C_{10}H_6OF_2$: C, 66.67; H, 3.36. Found: C, 66.06; H, 3.67.

Phenylcyclobutadienoquinone (XIII).[1b]—4,4-Difluoro-2-phenylcyclobutenone (XII) (200 mg.) was stirred with concentrated sulfuric acid (2 ml.) at 100°. Ice was added to the reaction mixture after 3 minutes. The precipitate was collected by filtration and recrystallized from acetone. The yellow crystals, m.p. 152°, gave no depression with an authentic sample of phenylcyclobutadienoquinone.

β-Piperidinostyrene.[16]—A solution of 9.2 g. of phenylacetaldehyde in 25 ml. of anhydrous benzene, a small crystal of *p*-toluenesulfonic acid and a solution of 7.0 g. of anhydrous piperidine were mixed. The solution turned hot and turbid instantaneously. It was boiled for 2 hr. in an open flask. The evaporating benzene which removed the eliminated water was replaced from time to time by anhydrous benzene. The reaction mixture was then evaporated *in vacuo* and yielded 15.9 g. of β-piperidinostyrene as a yellow oil. It was distilled under reduced pressure and yielded 7.5 g. of a yellow, low-melting solid, b.p. 95–100° at 0.02 mm.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.17; H, 9.20; N, 7.35.

The infrared spectrum of the product showed an extremely strong double bond absorption band at 6.1 μ.

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(16) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

BASEL, SWITZERLAND

[CONTRIBUTION FROM THE WM. H. NICHOLS CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

The Arylation of Cycloheptatriene

BY KARL WEISS AND SISTER MARIE LALANDE, C.S.J.

RECEIVED JULY 31, 1959

Phenyl-, *p*-chlorophenyl- and *p*-nitrophenylcycloheptatriene have been prepared by the direct arylation of cycloheptatriene under the conditions of the Meerwein reaction. The reaction was accompanied by the formation of cycloheptatrienylacetone. On the basis of spectral data and an analysis of the pertinent aspects of another synthesis of phenylcycloheptatriene, structures are proposed for the arylcycloheptatrienes obtained.

Interest in the radical chemistry of cyclic polyolefins has prompted us to investigate the arylation of cycloheptatriene, formally written as Ia, but preferably considered to be planar and pseudoaromatic.[1] The copper salt-catalyzed decomposition of diazonium salts in aqueous acetone (Meerwein reaction) was chosen as the radical source[2] since this system does not readily initiate the polymerization of olefins. The reaction of radicals with Ia can proceed in two ways, (i) by hydrogen abstraction from the methylene group and (ii) by

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(1) (a) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, THIS JOURNAL, **78**, 5448 (1956); (b) E. W. Abel, M. A. Bennett and G. Wilkinson, *Proc. Chem. Soc.*, 152 (1958).

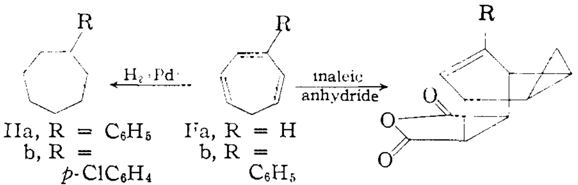
(2) (a) J. K. Kochi, THIS JOURNAL, **79**, 2942 (1957); (b) S. C. Dickerman, K. Weiss and A. K. Ingberman, *ibid.*, **80**, 1904 (1958).

addition to the double bond system. The first mode leads to the stabilized cycloheptatrienyl (tropyl) radical[3,4] which can dimerize, or react with other radicals or solvent. As far as radical addition is concerned, Ia has three non-equivalent vinylic positions, attack at any one of which can lead to products in which double bonds are conjugated with the substituent. In each case the formation of a further, non-conjugated isomer (7-aryl-1,3,5-cycloheptatriene) is possible by conjugative hydrogen abstraction from the intermediate radical.[5] Thus even without consideration of isomerization under the conditions of the experiment, all four possible arylcycloheptatrienes may result from direct arylation.

The procedure for the arylation of butadiene[6] was followed with minor modification for the phenylation, *p*-chlorophenylation and *p*-nitrophenylation of Ia. Nitrogen evolution took place rapidly and quantitatively at 25–40°, and the reaction evidently proceeded directly to the arylcycloheptatrienes which were isolated in low yields: phenylcycloheptatriene (Ib), 16%; *p*-chlorophenylcycloheptatriene (Ic), 29%; *p*-nitrophenylcycloheptatriene (Id), 7%.[7] Adducts containing aliphatic halogen[6] could in no case be isolated, even if the brief treatment of the crude reaction products with a tertiary amine, which was desirable in order to obtain absolutely halogen-free products, was omitted. The arylation was accompanied by the formation of the expected side-product (chloroacetone, aryl halide and arene), considerable amounts of higher boiling materials which were not further identified, and cycloheptatrienylacetone (Ie).

The aryl compounds were characterized by their spectra, quantitative hydrogenation to the arylcycloheptanes (IIa-c), and derivatization. The phenylcycloheptatriene was identical (refractive index and ultraviolet spectrum) with that prepared by Cope and D'Addieco from tropinone by a multi-step synthesis.[8]

Compound Ib absorbed 2.9 moles of hydrogen to form phenylcycloheptane (IIa), which was converted to the known mono- and diacetamido derivatives.[8,9] *p*-Chlorophenylcycloheptatriene was obtained as an almost colorless liquid which, like the phenyl analog, darkened slowly on standing in air, but could be stored under nitrogen without decomposition. Catalytic hydrogenation (3.2 moles) produced *p*-chlorophenylcycloheptane (IIb) and a small amount of hydrogenolysis product. The *p*-nitrophenyl compound Id[10] was isolated as an almost colorless, completely air-stable solid of m.p. 108–109° after recrystallization and vacuum sublimation. Its nature as an arylcycloheptatriene was established by hydrogenation (6.0 moles) and acetylation of the resulting *p*-aminophenylcycloheptane (IIc) to the same monoacetamide derivative prepared from phenylcycloheptane.



IIa, R = C_6H_5
b, R = *p*-ClC_6H_4
c, R = *p*-$NH_2C_6H_4$
d, R = CH_2COCH_3

Ia, R = H
b, R = C_6H_5
c, R = *p*-ClC_6H_4
d, R = *p*-$NO_2C_6H_4$
e, R = CH_2COCH_3

IIIa, R = H
b, R = C_6H_5
c, R = *p*-ClC_6H_4
d, R = *p*-$NO_2C_6H_4$

With maleic anhydride, Ib-d readily formed solid adducts IIIb-d, formulated in accordance with Alder and Jacobs' structure for the corresponding adduct of cycloheptatriene, IIIa.[12] Only one adduct could be isolated from each compound. However, the yields (IIIb, 42%; IIIc, 22%; IIId, 98%) indicate that the conversion was quantitative only with Id. It was found that IIIb resists hydrogenation in the presence of PtO_2, and that all three compounds (IIIb-d) are remarkably stable toward reagents such as bromine in carbon tetrachloride and neutral potassium permanganate solution.[13]

The vacuum fractionation of foreruns of Ib and Ic afforded a pale yellow liquid, b.p. 67–68° (0.5 mm.), which gave a positive iodoform test. The structural assignment of cycloheptatrienylacetone (Ie) for this compound followed from its infrared spectrum, from catalytic hydrogenation (3.0 moles) to cycloheptylacetone (IId), and from the ultraviolet spectrum of its 2,4-dinitrophenylhydrazone (λ_{max}^{MeOH} 361 mμ, log ε 4.37) which is indicative of a non-conjugated carbonyl function.[16,16a]

Whether the obtained arylcycloheptatrienes constitute mixtures or pure isomers poses an interesting problem. The sharp melting point of Id, unchanged by repeated recrystallization and sublimation, seems to indicate that in this case

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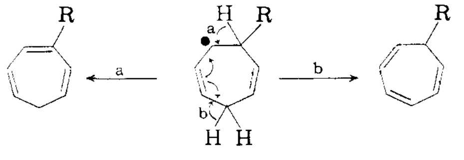
(3) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1954).

(4) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

(5) Even if hydrogen abstraction involves the prior oxidation (by cupric chloride) of the intermediate radical with subsequent loss of a proton,[2b] the possible modes may be formally represented as



Similar paths to conjugated and non-conjugated isomers may be written for radical attack at the other two positions.

(6) E. C. Coyner and G. A. Ropp, THIS JOURNAL, **70**, 2283 (1948).

(7) To indicate the gross structures at this point, Ib-e are arbitrarily shown as the 3-isomers, and IIIb-d as derived from these isomers.

(8) A. Cope and A. D'Addieco, THIS JOURNAL, **73**, 3419 (1951).

(9) H. Pines, A. Edeleanu and V. N. Ipatieff, *ibid.*, **67**, 2195 (1945).

(10) Arylcycloheptatrienes with dipolar negative substituents, such as Id, are not accessible by other methods which have furnished Ib, such as the reaction of tropylium salts with metal aryls[11] and Cope and D'Addieco's synthesis.[8]

(11) W. von E. Doering and L. H. Knox, THIS JOURNAL, **76**, 3203 (1954).

(12) K. Alder and G. Jacobs, *Ber.*, **86**, 1528 (1953).

(13) Similar double bond unreactivity is shown by the M.A. adducts of 1,1,4-trimethyl-2,4,6-cycloheptatrienes[14] and of ethyl norcaradienecarboxylate.[15]

(14) K. Alder, K. Kaiser and M. Schumacher, *Ann.*, **602**, 80 (1957).

(15) (a) G. O. Schenck and H. Ziegler, *ibid.*, **584**, 221 (1953); (b) K. Alder, H. Jungen and K. Rust, *ibid.*, **602**, 94 (1957).

(16) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

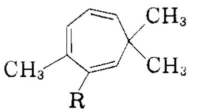
(16a) NOTE ADDED IN PROOF.—The properties of Ie correspond with those recently reported by K. Conrow, THIS JOURNAL, **81**, 5461 (1959), for cycloheptatrienyl acetone prepared from tropylium bromide.

TABLE I

Compound	λmax, mμ		log ε	
Ia[a]	261		3.54	
Ib[b,c]	232	285	4.17	3.94
Ib[d]	232	284	4.22	3.98
Ib[e]	236	290	4.17	3.80
Ib[f]	256		3.56	
Ic[b]	238	288	4.22	4.06
Id[b]	220[g]	268	4.05[g]	4.15
IV, R = H[h]	269		3.58	
IV, R = CH_3[h]	275		3.67	
IV, R = C_6H_5[h]	237		4.24	

[a] Ref. 17; solvent isoöctane. The spectrum of Ia has been variously reported as λ_{max} 266 mμ, log ε 3.62 (refs. 11 and 18) and λ_{max} 260 mμ (ref. 19). [b] This work; solvent methanol. [c] The spectrum is identical in cyclohexane. [d] From tropinone, ref. 8; solvent cyclohexane. [e] From biphenyl and diazomethane, ref. 18; solvent isoöctane. [f] 7-Phenyl-1,3,5-cycloheptatriene, ref. 11. [g] Shoulder. [h] Ref. 14.

we have indeed obtained a single isomer. Table I, which lists the pertinent ultraviolet spectra, shows that whereas the phenylcycloheptatriene prepared by us is spectroscopically identical with the product of Cope and D'Addieco, its spectrum differs somewhat from that of Ib prepared from biphenyl and diazomethane[18–20] and considerably



IV

from that of 7-phenyl-1,3,5-cycloheptatriene.[11] Unless this spectral coincidence is fortuitous,[21] the two products constitute identical isomers or mixtures of isomers. To assay the significance of this implication, we have reconsidered the relevant steps of Cope and D'Addieco's synthesis, which involves the Hofmann elimination or thermal decomposition of 3-phenyl-α-des-methyltropidine methiodide (VI), obtained from tropinone (V).[22]

If no isomerization occurs, the product is 3-phenyl-1,3,5-cycloheptatriene (VIIa). Isomerization can involve either VI or the final product. If we dismiss as unlikely the formation of a phenylcycloheptatrienyl anion[23] and the formation of isomers of VI in which the double bonds are not fully conjugated, or cross-conjugated, with the phenyl group, then Cope and D'Addieco's product is either VIIa or a mixture of VIIa and 1-phenyl isomer VIIb. It appears reasonable to conclude that the phenyl compound prepared by direct arylation and, by analogy, Ic and Id are similarly constituted.

The ultraviolet spectrum of Ic resembles closely that of Ib, but the spectrum of Id with its prominent peak at 268 mμ is more like those of unsubstituted cycloheptatriene, 7-phenylcycloheptatriene and IV (R = H or CH_3). Yet the extinction of Id is comparable with that of Ib and of Ic (log ε > 4). The sizable spectral shift shown by Id relative to the latter compounds is not unexpected, since it is known that the introduction of *p*-nitro groups into a phenyl-conjugated alkene can produce large spectral effects.[25] That IV (R = C_6H_5) does not absorb at higher wave lengths than IV (R = H) despite phenyl substitution at a vinylic position may, in part, be due to the conjugation-inhibiting steric effect of the adjacent methyl group.

The structural assignments find some further support in the infrared spectra of Ib-d and their maleic anhydride adducts IIIb-d. Thus Ib-d all show CH_2 stretching doublets at 2880 and 2820 cm.$^{-1}$, 2880 and 2820 cm.$^{-1}$, and 2940 and 2870 cm.$^{-1}$, respectively,[28] ruling out the 7-aryl structure for Id. Depending on the structure of the arylcycloheptatriene from which they are derived, the maleic anhydride adducts will differ in the degree of substitution at the double bond. Thus spectral evidence was sought for the trisubstituted ethylenic bond which is present in the adducts of 3-arylcycloheptatrienes, and absent in the adducts of the 1-, 2- and 7-isomers. In the hope of facilitating the interpretation of the spectra of IIIb-d, the spectrum of IIIa (the adduct of Ia) was also measured. The four spectra, which are characterized by a large number of sharp and intense bands,[29] show many similarities and, apart

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(17) W. von E. Doering and L. H. Knox, THIS JOURNAL, **79**, 352 (1957).

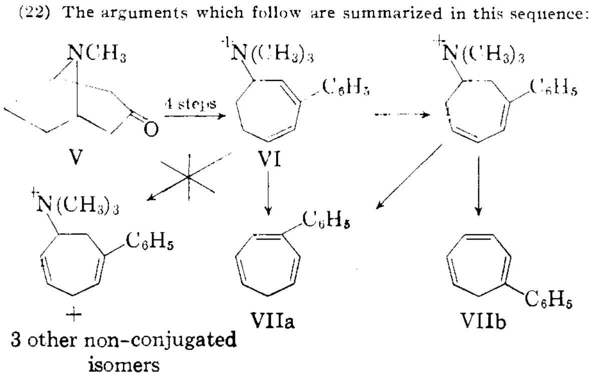
(18) W. von E. Doering and L. H. Knox, *ibid.*, **75**, 297 (1953).

(19) H. L. Dryden, *ibid.*, **76**, 2841 (1954).

(20) The m.p. of the M.A. adduct of our product (136–137°) also differs from that reported in ref. **18** (131–132°).

(21) Thus C. Grundmann and G. Ottmann, *Ann.*, **582**, 163 (1953), have found the spectra of 1,3,5- and 1,3,6-cycloheptatriene-1-carboxylic acids to be almost identical.

(22) The arguments which follow are summarized in this sequence:



The elimination reaction of anhydroecgonine[21] to produce approximately equimolar mixture of 1,4,6- and 1,3,6-cycloheptatriene-1-carboxylic acids[1a] represents an analogous situation. Although twelve structures can formally be written for the intermediate dimethylaminocycloheptadienecarboxylic acid,[21] it is significant that there are two structures, accessible from anhydroecgonine without rearrangement and having the double bonds fully conjugated or cross-conjugated with the carboxyl group, which lead to the observed mixture of acids.

(23) A triplet ground state has been calculated for the anion of Ia[3], and experimentally it was found that neither Ia nor esters of 1,3,5- and 1,3,6-cycloheptatrienecarboxylic acid undergo base-catalyzed condensations.[24]

(24) J. Thiele, *Ann.*, **319**, 226 (1901); C. Grundmann, G. Ottmann and G. Gollmer, *ibid.*, **582**, 178 (1953).

(25) Thus C. S. Rondestvedt, Jr., M. J. Kahn and O. Vogl, THIS JOURNAL, **78**, 6115 (1956), have reported that the long wave length bands of α-phenylmaleimides undergo hypsochromic shifts of 10–16 mμ when *p*-nitro groups are introduced. Also, the primary maxima in styrene and *p*-nitrostyrene appear at 244 mμ (log ε 4.23)[26] and 300 mμ (log ε 4.14),[27] respectively.

(26) Y. Hirschberg, THIS JOURNAL, **71**, 3241 (1949).

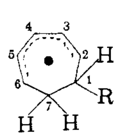
(27) M. J. Kamlet and D. J. Glover, *ibid.*, **77**, 5696 (1955).

(28) These bands appear at 2875 and 2830 cm.$^{-1}$ in Ia; see ref. 19.

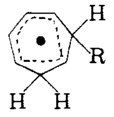
(29) E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.*, 4073 (1956), have also observed that the spectra of some bicyclo[2,2,1]heptane derivatives show many sharp, intense bands, ascribed by them to the rigidity of these molecules.

from absorptions due to substituents and to aromatic substitution patterns, differ mainly in the 900–650 cm.$^{-1}$ region; IIIa has strong bands at 739 and 743 (doublet), and 751 cm.$^{-1}$ which are probably associated with *cis*-ethylenic C–H deformations.[30] The spectrum of IIIb shows intense absorption at 692 and 702 (doublet), 718, and 761 cm.$^{-1}$, whereas IIIc and IIId have prominent bands at 737 and 747 cm.$^{-1}$, respectively, and only weak bands below 730 cm.$^{-1}$. Since IIIb is a monosubstituted benzene, strong absorption near 700 and 750 cm.$^{-1}$ is expected.[31] In the cases of IIIc and IIId, C–Cl and lower frequency C–NO$_2$ absorptions are anticipated, but there is considerable uncertainty regarding their positions. Compounds IIIb-d all have medium to strong peaks between 800–870 cm.$^{-1}$ (IIIb: 858, 841 and 822 cm.$^{-1}$; IIIc: 862, 848, 830 and 822 (doublet), and 803 cm.$^{-1}$; IIId: 863, 841, 821, and 803 cm.$^{-1}$), which includes the region where the trisubstituted ethylenic system usually shows absorption. The identification of this structural feature is, however, rendered problematical not only by the aromatic substitution bands expected in this range for IIIc and IIId, but also by the occurrence of strong bands at 853 and 833 cm.$^{-1}$ in the spectrum of IIIa. On the other hand, the latter two bands appear to be retained throughout the series IIIa-d and are probably represented by the higher frequency bands in IIIb-d. Therefore the appearance of one additional band in this region for IIIb, and two additional bands for IIIc and IIId is significant, and may be considered indicative of trisubstitution at the double band. These data are reconcilable with structures for IIIb-d derived from 3-aryl-1,3,5-cycloheptatrienes. The conversion of Id to IIId in 98% yield supports the contention that Id is not a mixture, but is the 3-aryl isomer. The lower isolated yields of IIIb (42%) and IIIc (22%) only permit the more limited suggestion that this isomer is present in Ib and Ic.

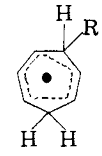
The failure to isolate halogen-containing adducts in the arylation of Ia contrasts with the behavior of other polyolefins.[6,32] Since, in general, olefins from addition products while aromatic compounds undergo substitution,[2b,33] this result may be taken as further evidence of the pseudo-aromatic nature of the cycloheptatriene system. The low yield of arylation product and the relative abundance of higher molecular weight materials undoubtedly reflect the strong tendency of the intermediate arylcycloheptadienyl radicals to dimerize,[34] or of the initial products to undergo further substitution. The formation of specific isomers can be rationalized in terms of more favorable transition states resulting from radical attachment at the 1- and 3-positions of Ia. Based on the reasonable assumption that the transition states closely resemble the intermediate radicals, the question of orientation may be considered qualitatively from the point of view of the stabilization derived from the delocalization of the odd electron.[35] The structures VIIIa, IXa and Xa, which represent attack at the 1-,2- and 3-positions of Ia, respectively, indicate in each case the conceivable overlaps of the remaining five *p*-orbitals. With attack in the 1-position, C$_2$,C$_3$,C$_4$,C$_5$ and C$_6$ can easily assume a planar arrangement (VIIIb) in which the orbitals can overlap quite efficiently for delocalization. In the case of attack in the 2- and 3-positions, delocalization utilizing all the *p*-orbitals would involve 1,3-interactions of the homoallylic type.[36] This non-adjacent overlap is a necessity for attack at the 2-position, if the odd electron is to be delocalized at all. However, the relatively strain-free conformation IXb in which C$_3$,C$_4$,C$_5$ and C$_6$ are coplanar is not favorable for the delocalization shown in IXa owing to the unsuitable disposition of the isolated *p*-orbital. Another, more twisted conformation of IXa (not shown) does not have C$_3$,C$_4$,C$_5$ and C$_6$ in one plane, but does offer the possibility of a diagonal overlap of the *p*-orbital on C$_1$ with the p-orbitals on C$_3$ and C$_6$. With radical attack at the 3-position the strainless conformation Xb is readily assumed in which, reminiscent of bicyclo[2,2,1]hepta-2,5-diene,[37] the orientation of the adjacent sets of p-orbitals is indicative of effective 1,3-overlap. While VIIIb is obviously important, the unique cyclic delocalization of the odd electron realizable in Xb can well be sufficiently more advantageous to lead to the preferred formation of 3-aryl isomers.



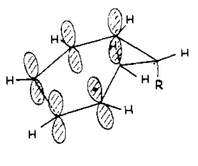
VIIIa



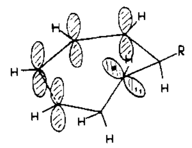
IXa



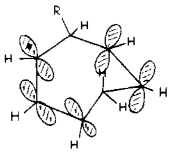
Xa



VIII b



IX b



Xb

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[30] The presence of anhydride and cyclopropane rings evidently exerts a considerable influence on the position of this absorption, since in the structurally related bicyclo[2,2,2]octene the corresponding bands appear at 715 (shoulder) and 700 cm.$^{-1}$; see J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, THIS JOURNAL, **77**, 594 (1955).

[31] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, chapters 3 and 5.

[32] E. Müller, *Angew. Chem.*, **61**, 179 (1949).

[33] S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).

[34] *Cf.* D. F. DeTar and R. A. J. Long, THIS JOURNAL, **80**, 4742 (1958).

[35] The molecular models described by A. S. Dreiding, *Helv. Chim. Acta*, **42**, 1339 (1959), proved to be particularly useful for this purpose.

[36] M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954).

[37] Although non-adjacent overlap is evidently not important in the ground state of bicyclo[2,2,1]heptadiene,[38] the reality of this mode of interaction in this molecule is illustrated by the formation of nortricyclene derivatives with a variety of ionic reagents.[39] With radical reagents, substituted nortricyclenes are also obtained, but there is evidence that a non-classical homoallylic radical is not involved[40]; see, however, footnote 27, ref. 40.

[38] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[39] S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956); L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **78**, 2819 (1956).

[40] S. J. Cristol, G. D. Brindell and J. A. Reeder, *ibid.*, **80**, 635 (1958).

The isolation, from a Meerwein reaction, of an acetonyl compound comparable to cycloheptatrienylacetone (Ie) has so far not been reported. While the formation of Ie may involve the acetonyl radical,[2b] a copper chloride-catalyzed alkylation of Ia by chloroacetone appears equally feasible.

We wish to thank the Shell Chemical Corporation for a generous supply of cycloheptatriene.

Experimental[41]

The cycloheptatriene (91.4%, the remainder mainly toluene) was redistilled before use (b.p. 65–66° (150 mm.)), and was stored under nitrogen.

Phenylcycloheptatriene (Ib).—Aniline (freshly distilled, 14.0 g., 0.15 mole) was dissolved in a mixture of concentrated hydrochloric acid (37.5 ml., 0.45 mole) and 15 ml. of water, and was diazotized with sodium nitrite (10.4 g., 0.15 mole) in 20 ml. of water in the presence of ice (15 g.). This diazonium solution was added over 20 minutes, under nitrogen, to a well-stirred mixture of acetone (200 ml.), $CuCl_2\cdot 2H_2O$ (3.3 ml. of 9 *M* solution, 0.03 mole) and cycloheptatriene (18.5 g., 0.20 mole). Nitrogen evolution commenced after a brief induction period, and the theoretical volume was evolved in 30–45 minutes. During the reaction, the temperature was kept at 35–40° by occasional cooling. The two-phase mixture was extracted with ether and the extracts were washed with water and dried over magnesium sulfate. After removal of the solvent the residual orange-red liquid was heated with redistilled quinoline (80 g.) at about 100° for 15 minutes. The mixture was taken up in ether, and washed with water, dilute sulfuric acid (to remove quinoline), dilute sodium hydroxide solution (to remove phenol), and finally again with water until neutral. Evaporation of the ether and vacuum distillation gave 1.92 g. of forerun, b.p. 53–72° (0.1 mm.), containing ketonic material (*vide infra*), and 3.95 g. (16%) of crude Ib, b.p. 79–93° (0.1 mm.). A fraction b.p. 100–160° (0.1 mm.) and the semi-solid residue were not further investigated.[42]

Redistillation of the Ib fraction afforded pure phenylcycloheptatriene as an almost colorless liquid, b.p. 57–59° (0.05 mm.), n^{25}_{D} 1.6203 (reported: for the product from tropinone,[8] n^{25}_{D} 1.6202; for the product from biphenyl and diazomethane,[18] n^{25}_{D} 1.6164–1.6213; for 7-phenyl-1,3,5-cycloheptatriene,[11] n^{25}_{D} 1.5867–1.5888). The infrared spectrum (liquid, 0.025-mm. cell) shows prominent bands at 3015, 2880 and 2820 (doublet), 1600, 1495, 1445 and 1435 (doublet), 1400, 1387, 1330, 1290, 1075, 1035, 917, 964, 876, 755 and 735 (doublet), and 711 and 698 (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.8; H, 7.2. Found: C, 92.9; H, 7.1.

Hydrogenation of Ib in absolute ethanol in the presence of 5% Pd-on-C resulted in the absorption of 2.9 moles of hydrogen. Evaporation of the solvent and distillation gave phenylcycloheptane (IIa), b.p. 76° (0.5 mm.), n^{25}_{D} 1.5303 (reported b.p. 80–82° (0.65 mm.),[8] n^{25}_{D} 1.5287,[8] 1.5290 and 1.5310[11]).

Acetamido derivatives of IIa were prepared by the method of Ipatieff and Schmerling.[43] The procedure for the monoacetamido derivative gave a mixture of the mono- and diacetamido compounds which was separated by fractional crystallization from aqueous ethanol and carbon tetrachloride-hexane mixtures. The pure compounds had m.p. 172–173° and 241–242°, respectively (reported[9] 173° and 241°).

***p*-Chlorophenylcycloheptatriene (Ic).**—The cold, filtered diazonium solution prepared from *p*-chloroaniline (38.2 g., 0.30 mole), concentrated hydrochloric acid (72.5 ml., 0.88 mole), 30 ml. of water, 30 g. of ice and 21.0 g. (0.30 mole) of sodium nitrite dissolved in 40 ml. of water was added to a mixture of acetone (300 ml.), 9 *M* cupric chloride solution (6.0 ml., 0.054 mole), anhydrous sodium acetate (24.0 g., 0.29 mole, in 30 ml. of water) and cycloheptatriene (44.0 g., 0.46 mole) as described previously. With the temperature maintained between 25–33°, the nitrogen evolution was complete in 60 minutes. The products were separated by ether extraction. Evaporation of the dried ether solution left a brown liquid which was dissolved in benzene (200 ml.), decolorized with Norit-A, and heated at about 100° with γ-collidine (75 g.) for 15–30 minutes. Distillation of the benzene under reduced pressure after removing the γ-collidine with dilute sulfuric acid left a colored liquid which was vacuum distilled. Two fractions were collected: (1) 3.0 g., b.p. 48–76° (0.05 mm.), containing a ketone; and (2) 17.5 g. (29%) of impure Ic, b.p. 92–124° (0.05–0.30 mm.). From the fractional redistillation of the second fraction, 15.0 g. of pure Ic was obtained as an almost colorless oil, b.p. 101–102° (0.1 mm.) and n^{25}_{D} 1.6302. Strong bands in the infrared spectrum (liquid, 0.025-mm. cell) appear at 3010, 2880 and 2820 (doublet), 1590, 1490, 1430, 1415, 1385, 1322, 1290, 1180, 1093, 1015, 967, 878, 830, 771, 741 and 731 (doublet), 719 (shoulder), 690 and 667 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{11}Cl$: C, 77.0; H, 5.5; Cl, 17.5. Found: C, 76.8; H, 5.5; Cl, 17.7.

Compound Ic (1.515 g.), in 35 ml. of absolute ethanol in the presence of 300 mg. of 5% Pd-on-C, absorbed 3.2 moles of hydrogen in 155 minutes. Evaporation of the solvent left 1.422 g. (91%) of impure ***p*-chloropenylcycloheptane (IIb)**, which was freed of traces of hydrogenolysis product by vacuum fractionation. The colorless liquid had b.p. 103–104° (0.5 mm.) and n^{25}_{D} 1.5420.

Anal. Calcd. for $C_{13}H_{17}Cl$: C, 74.8; H, 8.2; Cl, 17.0. Found: C, 75.3; H, 7.9; Cl, 16.9.

***p*-Nitrophenylcycloheptatriene (Id).**—*p*-Nitrobenzenediazonium chloride solution was prepared from *p*-nitroaniline (20.7 g., 0.15 mole), concentrated hydrochloric acid (45.0 ml., 0.54 mole), 15 ml. of water, and sodium nitrite (10.4 g., 0.15 mole) dissolved in 20 ml. of water. The cold, filtered solution was diluted to 150 ml. with water, and added slowly to a mixture of acetone (200 ml.), 9 *M* cupric chloride solution (3.3 ml., 0.03 mole) and cycloheptatriene (18.5 g., 0.20 mole). At 25–31°, the theoretical volume of nitrogen was evolved in 10 minutes. Most of the acetone was distilled under reduced pressure, and the two-phase residue was steam distilled until the distillate was clear. Filtration of the distillate gave 6.1 g. (26%) of *p*-nitrochlorobenzene, identified by m.p. and mixed m.p. The distillation residue was extracted with benzene, and the dried solution decolorized with Norit-A. The reddish, viscous liquid left after evaporation of the benzene was triturated with a small quantity of cold ether to give 1.70 g. of light yellow solid, m.p. 104–105°. Another 0.51 g. of material, m.p. 98–104°, was obtained from the mother liquor, bringing the yield of crude Id to 2.21 g. (7%). After recrystallization from aqueous methanol (85%) and vacuum-sublimation at 80° (0.1 mm.) the now almost colorless crystals had an m.p. of 108–109°; infrared spectrum (KBr): prominent bands at 3030, 2940 and 2870 (doublet), 1610, 1520, 1345, 1270, 1200, 1115, 1015, 1000, 946, 927, 856, 807, 757 and 745 (doublet), and 715 and 704 (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{11}NO_2$: C, 73.2; H, 5.2; N, 6.6. Found: C, 73.1; H, 5.4; N, 6.4.

Hydrogenation of 123 mg. of Id in 30 ml. of absolute ethanol over 37 mg. of 5% Pd-on-C resulted in the absorption of 6.0 molar equivalents of hydrogen in 90 minutes. The oily residue obtained by evaporation of the solvent was treated with acetic anhydride, and the resulting acetyl derivative was recrystallized from aqueous ethanol to give colorless plates, m.p. 172–173°, not depressed by admixture with the monoacetamido derivative of IIa.

Cycloheptatrienylacetone (Ie).—Vacuum fractionation of the fraction b.p. 48–76° (0.05 mm.) from the preparation of Ic gave 1.4 g. of pale yellow liquid, b.p. 67–68° (0.5 mm.), n^{25}_{D} 1.5244. The material gave a negative Schiff aldehyde test, and a positive iodoform test; infrared spectrum (liquid, 0.025-mm. cell): bands at 3010, 2890 (shoulder), 1700, 1600, 1520, 1395, 1350, 1275, 1230 and 1210 (doublet), 1155, 1035, 950, 745, and 715 and 693 (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.1; H, 8.2. Found: C, 80.8; H, 8.0.

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[41] All melting points are corrected, and boiling points uncorrected. Microanalyses by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Ultraviolet spectra were determined with a Beckman model DK-2 spectrophotometer, and infrared spectra with a Baird model 4-55 recording spectrometer.

[42] In another experiment the reaction product was distilled at initially higher pressure, without prior quinoline treatment and washing with base. Small amounts of benzene, chlorobenzene and phenol (identified as tribromophenol) were obtained as well as the fractions described.

[43] V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **59**, 1056 (1937).

Compound Ie (195 mg.), dissolved in ethanol and treated with a slight excess of 2,4-dinitrophenylhydrazine in phosphoric acid,[44] gave 400 mg. (90%) of the **2,4-dinitrophenylhydrazone**, m.p. 170–171° after recrystallization from ethanol; ultraviolet spectrum: $\lambda_{\max}^{\text{MeOH}}$ 361 mμ, log ε 4.37; 352 mμ (shoulder), log ε 4.16; 229 mμ, log ε 4.24.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.5; H, 4.9; N, 17.1. Found: C, 58.3; H, 4.7; N, 17.0.

Ketone Ie (538 mg.) in ethanol in the presence of 5% Pd-on-C (113 mg.) absorbed 3.0 moles of hydrogen in 65 minutes. Evaporation of the solvent and distillation afforded **cycloheptylacetone** (IId) as a colorless liquid, b.p. 54–55° (0.5 mm.), n^{25}D 1.4629; infrared spectrum (liquid, 0.025-mm. cell): peaks at 2930, 1715, 1465 and 1454 (doublet), 1405, 1352, 1270, 1235, 1183, 1155 and 953 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.9; H, 11.8. Found: C, 78.7; H, 11.9.

The 2,4-dinitrophenylhydrazone of IId was obtained in 93% yield, m.p. 125–126° after recrystallization from aqueous ethanol; ultraviolet spectrum: $\lambda_{\max}^{\text{MeOH}}$ 362 mμ, log ε 4.49; 264 mμ (shoulder), log ε 4.14; 230 mμ, log ε 4.34.

Anal. Calcd. for $C_{16}H_{22}N_4O_4$: C, 57.5; H, 6.6; N, 16.8. Found: C, 57.9; H, 6.9; N, 16.7.

Compound Ie was also obtained by distillation of the forerun from the preparation of Ib. The pale yellow liquid had a b.p. of 52–55° (0.1 mm.), but its infrared spectrum showed bands (particularly at 818, 797 and 780 cm.$^{-1}$) not present in the spectrum of pure Ie. A sulfur-containing impurity was found to be present, arising from the quinoline used in the preparation of Ib. The 2,4-dinitrophenylhydrazone prepared from the impure ketone was identical with that described above.

Maleic Anhydride Adducts IIIa-d.—With the exception of IIIa, these were prepared by refluxing equimolar amounts of triene and maleic anhydride in dry benzene for 24 hours.[18]

(a) **Compound IIIa from Cycloheptatriene.**—This compound was prepared as described by Kohler, *et al.*[45] Three recrystallizations from hexane gave colorless needles, m.p. 103–104° (reported 102–104°,[39] 104–105°[19]). The infrared spectrum (KBr) shows strong bands at 3025, 2960, 1870 and 1840 (doublet), 1800, 1237, 1105, 1090, 1004, 972, 958 and 953 (doublet), 929, 918 (shoulder), 853, 833, 741, 743 and 739 (doublet) cm.$^{-1}$.

(b) **Compound IIIb from Phenylcycloheptatriene.**—The adduct was isolated by the addition of pentane. The crystals, m.p. 128–133° (42%), were recrystallized twice from benzene–pentane to furnish colorless needles, m.p. 136–137° (reported[18] for the adduct of Ib from biphenyl and diazomethane, 131–132°); infrared spectrum (KBr): prominent peaks at 3040, 2960, 1830, 1760, 1480, 1430, 1225, 1087 and 1070 (doublet), 1037, 997, 958 and 948 (doublet), 921, 858, 841, 822, 761, 718, 702 and 692 (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3; mol. wt., 266. Found: C, 76.6; H, 5.3; mol. wt., 278.

(c) **Compound IIIc from *p*-Chlorophenylcycloheptatriene.**—The turbid solution resulting from the addition of pentane to the cooled reaction mixture deposited crystals, m.p. 120–125° (22%), on standing in the cold for several weeks. Three recrystallizations from benzene–pentane gave colorless prisms, m.p. 129–130°; infrared spectrum (KBr): prominent bands at 3000, 1855, 1775, 1485, 1225 (shoulder), 1215, 1095, 1073, 1010 and 1003 (doublet), 947, 922 (shoulder), 918 and 903 (doublet), 862, 848, 830 and 822 (doublet,) 803 and 737 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{13}ClO_3$: C, 67.9; H, 4.4; Cl, 11.8. Found: C, 68.1; H, 4.1; Cl, 11.7.

From the attempted hydrogenation, at atmospheric pressure, of IIIb in ethyl acetate in the presence of PtO_2 only unchanged starting material, identified by mixture m.p. and infrared spectrum, could be isolated.

(d) **Compound IIId from *p*-Nitrophenylcycloheptatriene.**—The reaction mixture began to deposit crystals after a few hours of heating. Filtration gave the adduct in 98% yield, m.p. 238–239°. The colorless prisms obtained by three recrystallizations from ethyl acetate had the same melting point; infrared spectrum (KBr): prominent bands at 3050, 2940, 1850, 1770, 1595, 1520, 1340, 1223, 1105, 1081, 1061, 989, 920, 887, 863, 841, 821, 803 and 747 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{13}NO_5$: C, 65.6; H, 4.2; N, 4.5. Found: C, 65.3; H, 4.3; N, 4.7.

New York 53, N. Y.

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[44] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 316.

[45] E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, This Journal, **61**, 1057 (1939).

[Contribution from the Department of Chemistry, Fordham University, New York, 58, N. Y.]

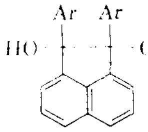
Oxidation Kinetics of *vic*-Diols in Cyclic Systems. II.[1a] Lead Tetraacetate Oxidation of *cis*- and *trans*-1,2-Diaryl-1,2-acenaphthenediols[1b]

By Emil J. Moriconi, William F. O'Connor, Elizabeth A. Keneally and
Frederick T. Wallenberger

Received September 3, 1959

The rates of oxidation with lead tetraacetate in acetic acid are reported for a series of *cis*- and *trans*-1,2-diaryl-1,2-acenaphthenediols which varied in bulk and electronic effects [aryl = phenyl (Ia), 4-methylphenyl (Ib), 2,4-dimethylphenyl (Ic), 2,4,6-trimethylphenyl (Id) and α-naphthyl (Ie)]. *cis*-I (H), *cis*-II (methyl), *cis*-Ia and *cis*-Ie diols, and all the *trans*-diols showed true second-order kinetics. *cis*-Ib and *cis*-Ic diols at 20°, and *cis*-Ie diol at 40° simultaneously underwent a partial pinacol rearrangement. Rate retardation was observed in the lead tetraacetate oxidations of *trans*-Ia, *trans*-Ib and *trans*-Ic diols in relatively non-polar 99% benzene–1% acetic acid and is suggestive of an acyclic mechanism. All other diols can be mechanistically accommodated by Criegee's cyclic intermediate or cyclic transition state. There was no correlation between reaction rates and intramolecular hydrogen bond strengths.

Recently[2] we reported on the synthesis and intramolecular hydrogen bonding measurements of a series of *cis*- and *trans*-1,2-acenaphthenediols in which the 1,2-aryl substituents varied in bulk and electronic effects.



I, Ar = H
Ia, Ar = phenyl
Ib, Ar = 4-methylphenyl (*p*-tolyl)
Ic, Ar = 2,4-dimethylphenyl (*m*-xylyl)
Id, Ar = 2,4,6-trimethylphenyl (mesityl)
Ie, Ar = α-naphthyl

Both *cis*- and *trans*-diols displayed high frequency bands (3584–3600 cm.$^{-1}$) which were as-

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[1] (a) Part I, E. J. Moriconi, F. T. Wallenberger and W. F. O'Connor, This Journal, **80**, 656 (1958); (b) Presented in part at the Meeting-in-Miniature, Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1958, and at The 134th Meeting of The American Chemical Society, Chicago, Ill., September, 1958.

[2] E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally and F. T. Wallenberger, This Journal, **81**, 6472 (1959).