

Methylenecyclopropenes. I

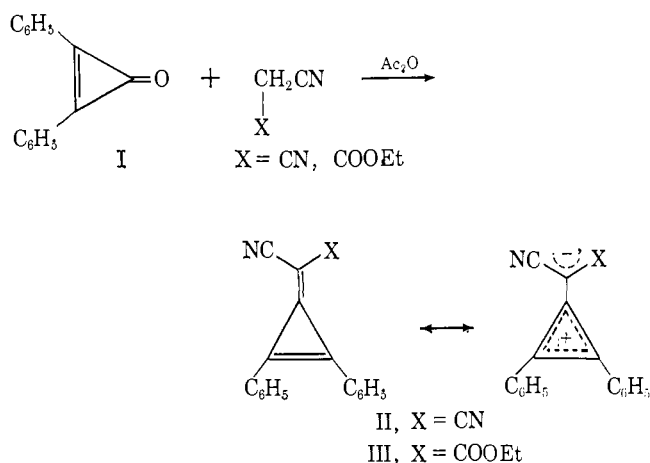
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Contribution No. 1059 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware. Received March 1, 1965

1,2-Diphenyl-3-dicyanomethylenecyclopropene and 1,2-diphenyl-3-(carbethoxycyanomethylene)cyclopropene have been prepared, and their physical properties have been determined. Chlorination of these systems occurs exclusively at the external double bond to give 1,2-diphenyl-3-chloro-3-(chlorodicyanomethyl)cyclopropene and 1,2-diphenyl-3-chloro-3-(carbethoxychlorocyanomethyl)cyclopropene.

Small-ring systems containing double bonds in unusually restricted orientations at close range have long been of considerable interest¹ but were inaccessible by normal routes.² Of particular interest is the methylenecyclopropene system with an estimated freevalence index of 0.97 at the methylene position.¹ In view of the known stability of cyclopropenium ions,³ substitution at the methylene position by electronegative substituents should create considerable charge separation resulting in appreciable stabilization of the pseudoaromatic structure. In this paper, we describe the synthesis and properties of the methylenecyclopropenes II and III. During our investigation of the chemistry of these systems, four communications reporting various methylenecyclopropenes appeared.⁴

Refluxing a solution of diphenylcyclopropenone⁵ (I) and malononitrile or ethyl cyanoacetate in acetic anhydride containing catalytic amounts of an amphoteric compound such as β -alanine results in the formation of



(1) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(2) E.g., R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

(3) See, e.g., F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964); R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(4) (a) M. A. Battiste, *ibid.*, **86**, 942 (1964); (b) W. M. Jones and J. M. Denham, *ibid.*, **86**, 944 (1964); (c) E. D. Bergmann and I. Agranat, *ibid.*, **86**, 3587 (1964); (d) A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964).

(5) R. Breslow, J. Posner, and A. Krebs, *ibid.*, **85**, 234 (1963); R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

the methylenecyclopropenes II and III in 24% and 14.6% yields, respectively. In the absence of a catalyst, the yields are significantly diminished.⁶ *cis*- α -Phenylcinnamic acid accompanies the formation of II, possibly the result of addition of the acetic acid produced in the reaction to the carbonyl group followed by ring opening *via* protonation of the double bond. No α -phenylcinnamic acid was obtained when II was subjected to the reaction conditions. The conditions selected for the condensations are similar to those employed with tropone,^{7a} affording an interesting comparison of the two ketones.

The structures of II and III are in accord with all structural data. II shows infrared bands at 2203, 2188 (conjugated C \equiv N), 1862, and 1597 and 1575 cm.⁻¹ which have been assigned to the internal and external double bonds, respectively.^{4,7b}

Although such an assignment might appear attractive on the basis of a large contribution from the dipolar structure, the assignment of the corresponding bands in diphenylcyclopropenone (I) has been highly controversial,^{5,7b,7c} with arguments presented for both possible assignments.^{7b,7c}

Recently, a normal coordinate analysis of diphenylcyclopropenone (I) and its Raman spectrum have shown that it is incorrect to assign either frequency to a pure carbonyl or a pure cyclopropene vibration in I because the modes of vibration are heavily mixed.^{7d} The results^{7d} are consistent with considerable charge separation and indicate that, without such mixing, both vibrations would occur in the neighborhood of 1750 cm.⁻¹. Similar conclusions should be drawn with regard to II and III in which the vibrations of the two unsaturated functions undoubtedly interact strongly.^{7e} The ultraviolet spectrum in acetonitrile showed λ_{\max} 347 m μ (ϵ 13,750) and 298 m μ (ϵ 28,300), while the longest wave length absorption in the starting ketone appears as a shoulder at 316 m μ . The molecular weight was determined by vapor pressure osmometry in chloroform and by mass spectroscopy by direct introduction of the sample into the isatron. The parent ion (m/e 254) was the most abundant species, the M +

(6) (a) *Cf.* ref. 4c; (b) *cf.* the aldol condensation involving both an acid and a base: R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter IX.

(7) (a) Y. Kitahara and K. Doi, Japanese Patent No. 13071 (1962). (b) A cyclopropene double bond bearing two phenyl groups has a characteristic absorption band at 1820 cm.⁻¹: R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2732 (1963); also *cf.* ref. 3 and A. W. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 18 (1965). (c) See, e.g., R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); D. N. Kursanov, M. E. Volpin, and Yu. D. Koreskov, *Izv. Acad. Nauk SSSR, Otd. Khim. Nauk*, 560 (1959); R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960); Yu. G. Borodka and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **136**, 1335 (1961). (d) Professor R. C. Lord, personal communication. (e) When two vibrational levels of nearly the same energy are coupled, one is shifted up and the other down in energy corresponding to a mixing of the normal coordinates of the two uncoupled levels: G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., Princeton, N. J., 1960, Chapter II.

1 and M + 2 ions showing close correspondence with the calculated intensity based on natural isotopic abundances⁸ for the empirical formula C₁₈H₁₀N₂. Similar agreement was observed in the mass spectrum of III at *m/e* values of 301, 302, and 303.

Catalytic hydrogenation of II (palladium on charcoal) resulted in consumption of 1.8 equiv. of hydrogen, but the resulting tetrahydro derivative could not be isolated.

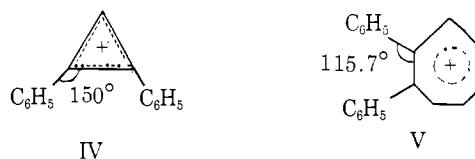
N.m.r. Spectra. Valuable structural data was provided by the lower melting, more soluble system III. The aromatic n.m.r. absorption provides compelling evidence for the charge separation in III and indicates near coplanarity of the phenyl rings.

The n.m.r. spectrum of III in deuteriochloroform shows the *ortho* hydrogen multiplet centered at τ 1.62 (area 2) and the *meta* and *para* hydrogen⁹ resonance at 2.36 (area 3). The ethyl group quadruplet-triplet absorption appeared at τ 5.63 (2) and 8.62 (3), respectively.

When a phenyl ring can achieve coplanarity with an electron-withdrawing substituent, the aromatic hydrogens are not only strongly deshielded, but also become differentiated into an AB₂C₂-type pattern with the *ortho* hydrogens invariably appearing at lowest field. Thus, nitrobenzene and benzaldehyde show unsymmetrical multiplets assigned to the *ortho* hydrogens at -0.97 and -0.73 p.p.m., respectively, from benzene.¹⁰ The *meta* and *para* hydrogens occur in a grouping at -0.2 to -0.4 p.p.m. Since the *para* proton may be identified with the strongest peak in the spectrum,¹¹ it may be shown that the *para* hydrogen is also at lower field than the *meta* hydrogens, as expected on the basis of charge densities in the ring.

However, more pertinent models are provided by diphenylcyclopropenium ion (IV)⁹ and phenyltropylium ion¹² which show *ortho* hydrogen multiplets at τ 1.6 (extrapolated) and 1.9 (in acetonitrile), respectively, and *meta* and *para* hydrogen resonance at 1.9 (extrapolated) and 2.2, respectively. Two phenyl rings on adjacent positions of tropylium ion (V) apparently are forced out of coplanarity by virtue of the much smaller external angle (115.7°) subtended by an external bond from a planar, seven-membered ring relative to a planar, three-membered ring.¹³ The absence of appreciable charge delocalization into the phenyl ring in V¹⁴ is reflected as a single sharp phenyl

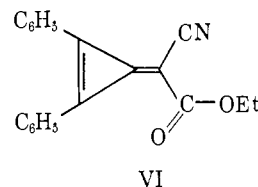
resonance in V with no differentiation between *ortho*, *meta*, and *para* hydrogens. Even more striking is the



fact that the chemical shift of the phenyl peak (τ 2.57) is close to that of benzene. Similarly, anilinium ion, in which resonance interaction with the ring cannot occur, shows a single peak (τ 2.47)¹⁵ shifted downfield only slightly from benzene.

Although *pK_a* data have indicated that phenyl groups stabilize cyclopropenium ions by conjugation to a relatively small extent,⁹ the delocalization must be large enough to account for the n.m.r. data. The exact magnitudes of the downfield shifts, particularly of the *ortho* protons, are a function of other factors in addition to charge density considerations. Deshielding by ring currents in the adjacent planar phenyl groups as well as in the cyclopropenium system should be significant. Definite conclusions regarding rotational freedom around the exocyclic double bond in III cannot be made from the n.m.r. data obtained thus far. In principle, such restricted rotation could result in different shielding parameters for the *ortho* hydrogens in one ring compared to those in the other ring.

Dipole Moment. The dipole moment of III (5.90 ± 0.1 D) determined in benzene at 25° is consistent with considerable charge separation in the ground state. This value may be compared with the moment of ω -cyano- ω -carbethoxyheptafulvene (μ = 4.40 D. in benzene)¹⁶ and is consistent with an average conformation represented by VI as opposed to the alternative planar carbethoxy rotamer of VI for reasons similar to



those applied to the heptafulvene system.¹⁶ Interestingly, in dioxane the values for II and ω,ω -dicyanoheptafulvene are much closer in magnitude (7.9^{4c} at 30° and 7.5¹⁶ at 25°, respectively).

Additions of fluoroboric or hydrobromic acids to acetonitrile solutions of II and III did not alter the ultraviolet spectra significantly. Apparently, they are not protonated under these conditions. This behavior may be contrasted with the facile protonation of 1,2-diphenyl-3-(carbethoxymethylene)cyclopropene.^{4a}

Chlorinations. Compounds II and III react smoothly and quantitatively with 1 equiv. of chlorine to give the dichloro derivatives VII and VIII, respectively. The ultraviolet spectra of VII and VIII are similar to those of diphenylcyclopropenium ion¹⁷ or diphenylalkoxy-

(8) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 61; J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, Chapter 8.

(9) Cf. R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

(10) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 258.

(11) P. L. Corio and B. P. Dailey, *J. Am. Chem. Soc.*, **78**, 3043 (1956); P. Diehl, *Helv. Chim. Acta.*, **44**, 829 (1961).

(12) A. Cairncross, Ph.D. Thesis, Yale University, 1963.

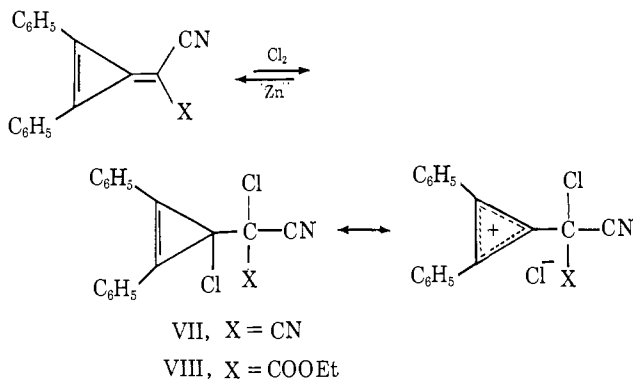
(13) The corresponding angle on cyclopropene, as determined by microwave spectra, is 149° 55': P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). Although the phenyl groups are twisted out of the plane at an average angle of 21° in *sym*-triphenylcyclopropenyl perchlorate crystals, this geometry probably does not apply in solution: M. Sundaralingam and L. H. Jensen, *J. Am. Chem. Soc.*, **85**, 3302 (1963).

(14) Although the ultraviolet spectra of V and 1,3- and 1,4-diphenyltropylium ions¹² are very broad, showing longest wave length λ_{\max} at 400, 368, and 399 μ , the corresponding extinction coefficients (log ϵ 3.77, 4.38, and 4.55, respectively) increase significantly in the 1,3- and 1,4-isomers.

(15) P. Isobe, T. Ikenone, and G. Hazato, *J. Chem. Phys.*, **30**, 1371 (1959).

(16) M. Yamakama, H. Watanabe, T. Mukai, T. Nozoe, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5665 (1960).

cyclopropenes,¹⁷ a fact indicative of some charge separation illustrated and serving to assign the chlorine addition to the external double bond. For example, VII shows λ_{\max} 299 $m\mu$ (ϵ 33,167), 314 (23,412), and 347 (1950), while 1,2-diphenyl-3-ethoxycyclopropene absorbs at 295 $m\mu$ (ϵ 30,000) and 315 $m\mu$ (ϵ 22,000). Diphenylcyclopropenyl cation, however, has similar absorption at 293 $m\mu$ (ϵ 30,400) and 306 $m\mu$ (ϵ 31,200).¹⁷ The proton n.m.r. spectrum of VII in deuteriochloroform showed absorption at τ 2.18 (2) and 2.40 (3), in agreement with some charge delocalization into the phenyl groups as discussed earlier. Interestingly, a second equivalent of chlorine does not add in the

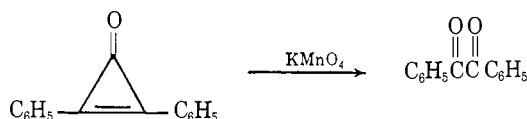


presence of excess halogen, a fact in accord with the predicted stability of the dipolar compounds VII and VIII, although steric factors should also inhibit the latter addition.^{7b}

Although the properties of compounds VII and VIII resemble the covalent 1,2-diphenyl-3-ethoxycyclopropene and diphenylcyclopropenyl cyanide,^{7b} the ultraviolet spectra are not definitive on this point. Contributions from the dipolar structures evident in the ionic diphenylcyclopropenyl bromide^{7b} must be significant in VII and VIII.

Dechlorination of VII and VIII takes place readily in the presence of zinc or under much milder conditions. Infrared spectra of VII and VIII could not be obtained in KBr pellets because of the facile reversion to II and III. This facile loss of chlorine is reminiscent of the behavior of diphenylcyclopropenone hydrohalide salts which lose HX under vacuum.¹⁸

Attempts to oxidize I or II to diphenyl triketone¹⁹ using potassium permanganate in acetone were unsuccessful. Instead, benzil was obtained from I in 20% yield.



Experimental

1,2-Diphenyl-3-dicyanomethylenecyclopropene. To 0.67 g. (3.25 mmoles) of diphenylcyclopropenone and

(17) R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2378 (1961).

(18) D. N. Kursanov, M. E. Vol'pin, and Y. D. Koreshkov, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 2855 (1960); *Zh. Obshch. Khim.*, **30**, 2877 (1960); R. A. Peterson, University Microfilms, Inc., Ann Arbor, Mich., microfilm No. 62-4245; *Dissertation Abstr.*, **23**, 1517 (1962).

(19) L. A. Bigelow and R. S. Hanslick, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 244.

0.25 g. (3.8 mmoles) of malononitrile in 3.5 ml. of acetic anhydride was added 0.01 g. of β -alanine. The mixture was refluxed for 2 hr. and allowed to cool overnight. The mixture was chilled in an ice bath and filtered to collect 0.17 g. (19.5%) of essentially pure yellow crystals. Recrystallization from acetonitrile gave product, m.p. 288–290° dec.

The infrared spectrum (KBr pellet) showed strong absorption at 2203, 2188, 1862, 1597, 1575, 1502, 1477, 1443, and 1393 cm^{-1} . Aromatic C–H stretching absorption appeared at 3058 with monosubstituted aromatic bands at 768 and 688 cm^{-1} .

The ultraviolet spectrum in acetonitrile showed λ_{\max} 347 $m\mu$ (ϵ 13,750), 298 (28,300), 286 (30,300), 267 (28,600), 261 (26,600 sh), 252 (21,250 sh), 237.5 (18,600), 230 (17,250), and end absorption at 220 $m\mu$.

Anal. Calcd. for $C_{15}H_{10}N_2$: C, 85.02; H, 3.96; N, 11.02; mol. wt., 254.27. Found: C, 85.39; H, 3.74; N, 11.04; mol. wt., 254 (mass spectrometry), 250 (vapor pressure osmometry in $CHCl_3$).

When the above preparation was repeated using 20 g. of diphenylcyclopropenone, a 24% yield of I was obtained.

Evaporation to dryness of the filtrate from a run using 5.0 g. of ketone and sublimation of the residue at 198° (0.1 mm.) gave 2.3 g. of white sublimate. From a 0.5-g. sample of sublimate was isolated 0.08 g. of *cis*- α -phenylcinnamic acid, m.p. 169–171° (lit.^{18,20} m.p. 172°). The infrared spectrum was identical with that of an authentic sample.

Hydrogenation. A mixture of 0.0932 mg. of 1,2-diphenyl-3-dicyanomethylenecyclopropene, 15 mg. of palladium on charcoal, 50 mg. of sodium carbonate, and 25 ml. of ethanol absorbed 0.0318 mg. of H_2 per milligram of sample, indicating reduction to the extent of 1.8 double bonds per molecule. Attempts to isolate the reduced material were unsuccessful.

1,2-Diphenyl-3-(cyanocarbethoxymethylene)cyclopropene. A mixture of 5.0 g. (0.025 mole) of diphenylcyclopropenone and 4.5 g. (0.04 mole) of ethyl cyanoacetate in 30 ml. of acetic anhydride containing a trace of β -alanine was refluxed for 3 hr. under dry nitrogen. The hot homogeneous solution was allowed to cool slowly and finally chilled in ice. Filtration gave 1.1 g. (14.6%) of the title compound, m.p. 148–156°. Recrystallization from benzene-hexane (1:1) gave a sample, m.p. 159–160°.

The infrared spectrum (KBr) showed strong absorption at 2198, 1852, 1681, and weaker absorption at 1595, 1575, and 1490 cm^{-1} . C–H stretching absorption appeared at 3058 (aromatic) and 2985 and 2899 cm^{-1} (saturated). Other bands appeared at 1477, 1445, 1277, 1143, 1099, 1092, 1081, 1067, 765, 756, 693, and 688 cm^{-1} .

The proton n.m.r. spectrum in deuteriochloroform (tetramethylsilane, internal reference) showed bands at τ 1.62 (area 4), 2.26 (area 6), a CH_2 quartet at 5.36 (area 2), and a CH_3 triplet at 8.62 (area 3), $J_{CH_2CH_3} = 7$ c.p.s.

Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.02; N, 4.65; mol. wt., 301.33. Found: C, 79.36; H, 4.98; N, 4.39; mol. wt., 301 (mass spectrometry), 318 (boiling point in benzene).

(20) R. E. Buckles and E. A. Hausman, *J. Am. Chem. Soc.*, **70**, 415 (1948). The *cis* designation refers to the two phenyl groups.

1,2-Diphenyl-3-chloro-3-(chlorodicyanomethyl)cyclopropene. Into a mixture of 0.1 g. (0.39 mmole) of 1,2-diphenyl-3-dicyanomethylenecyclopropene in 10 ml. of acetonitrile was introduced a slow stream of chlorine gas. Immediate reaction occurred, and the starting material dissolved completely. After adding an excess of chlorine, the mixture was evaporated to dryness on a rotary evaporator leaving an essentially pure white crystalline solid (0.091 g.). Recrystallization from benzene-hexane gave crystals, m.p. 118–120°. The infrared spectrum (CCl₄) showed weak absorption at 2250, 1820, and 1600, and stronger bands at 1450, 1335, 1170, 1100, 1010, 918, and 877 cm.⁻¹. The yields varied from 89 to 92%.

Anal. Calcd. for C₁₈H₁₀Cl₂N₂: C, 66.48; H, 3.10; N, 8.61; Cl, 21.80. Found: C, 66.11; H, 3.14; N, 8.60; Cl, 21.25.

The ultraviolet spectrum in acetonitrile showed λ_{\max} 347 m μ (ϵ 1950), 314 (23,412), 299 (33,167), 287 (26,014 sh), 277 (19,835 sh), 228 (21,786), and 220 (23,087).

1,2-Dicyano-3-chloro-3-(carbethoxychlorocyanomethyl)cyclopropene. In the manner described above, 0.2 g. (0.655 mmole) of 1,2-dicyano-3-(cyanocarbethoxymethylene)cyclopropene in 10 ml. of acetonitrile was combined with chlorine to give 0.233 g. (94.3%) of the title compound, m.p. 118–123°. Recrystallization

from benzene-hexane gave product, m.p. 116–118.5°.

The infrared spectrum in chloroform showed strong carbonyl absorption at 1770 cm.⁻¹. The ultraviolet spectrum in acetonitrile showed λ_{\max} 350 m μ (ϵ 7080), 295 (22,650), 267 (15,800), 240 (13,400), 228 (12,850), and 220 (13,000).

Anal. Calcd. for C₂₀H₁₅Cl₂NO₂: C, 64.53; H, 4.06; N, 3.76; Cl, 19.05. Found: C, 64.88; H, 4.21; N, 3.48; Cl, 19.09.

Mass Spectrum of 1,2-Diphenyl-3-dicyanomethylene-cyclopropene. Since this spectrum was obtained by direct introduction of the sample into the isatron, the intensities throughout the duration of the scan were not reproducible. In addition to the most abundant parent ion, other intense peaks occurred at the following *m/e* values with the approximate relative abundances parenthesized: 256 (2.1%), 255 (20.3%), 254 (100%), 227 (24.9%), 226 (12.1%), 100 (15.8%), 77 (11.4%), 63 (12.8%), 51 (32.9%), 50 (12%), and 39 (19.3%).

Mass Spectrum of 1,2-Diphenyl-3-(cyanocarbethoxymethylene)cyclopropene. The *M* + 1 and *M* + 2 peaks with abundances relative to the parent peak (*m/e* 301) were 302 (22.0%) and 303 (2.2%). Calculated intensities based on natural isotopic abundances were 21.8 and 2.3%, respectively. Other prominent peaks were observed at these *m/e* values: 273, 256, 229, 228, 227, 178, and 77.

Homolytic Abstraction of Benzylic Hydrogen

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Contribution from the Department of Chemistry, Southwestern at Memphis, Memphis, Tennessee 38112. Received May 3, 1965

*The rates of abstraction of benzylic hydrogen from *m*- and *p*-methyl-, *m*- and *p*-chloro-, *p*-bromo-, *p*-phenoxy-, and *p*-cyano-substituted toluenes were measured relative to toluene. For the reaction with *t*-butoxy radicals generated from *t*-butyl hypochlorite a better correlation was obtained with σ -substituent constants (ρ , -0.75) than with σ^+ . The *p*-phenyl group was found to deviate from this correlation only slightly but gave considerable deviation for the reaction with bromine atom. These results are discussed in terms of resonance stabilization of the incipient benzylic radical.*

Introduction

The formation of substituted benzylic radicals by abstraction of hydrogen by bromine¹ and chlorine² atoms, *t*-butoxy radicals,³ trichloromethyl radicals,⁴ and peroxy radicals² has been found to obey the Hammett $\rho\sigma$ relationship. Better correlations in all cases except the *t*-butoxy radical have been obtained with σ^+ rather than σ ,⁵ but Russell and Williamson²

have pointed out that the proper substituents for a clear distinction have not been investigated for the *t*-butoxy radical. With at least one abstracting species, the phenyl radical,⁶ little or no polar effect is observed. We have re-examined the competitive abstraction of benzylic hydrogen using *t*-butyl hypochlorite as a source of *t*-butoxy radical including selected *para*-substituted toluenes having significantly different σ - and σ^+ -constants.

The *p*-phenyl substituent does not give a good fit with the Hammett equation using standard substituent constants.⁷ We have examined the effect of this group in the abstraction reaction using both bromine atom and *t*-butoxy radical as examples of abstracting species giving large and small ρ -values.

Experimental

Materials. Reagent grade commercial toluene, benzene, and cyclohexane were distilled from sodium as constant-boiling heart cuts. *p*-Bromotoluene, *m*-chlorotoluene, and *p*-chlorotoluene were commercial, reagent grade materials. They were distilled taking constant-

(1) R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963).

(2) G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1964).

(3) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

(4) E. S. Huyser, *ibid.*, **82**, 394 (1960).

(5) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

(6) R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

(7) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).