thyl splittings arise from the 10 and 11 positions, as numbered in Chart I.

The calculations on V demonstrate quite clearly that the 4.2-G splitting in **2b** comes from the α-naphthyl proton (position 12 in Chart I). The calculations also predict that ρ_N in V is extremely close to ρ_N in IV, for identical values of k_{CN}. The A^N values for **1b** and **2b** are very close.

In view of our experimental results and the calculations shown above, Buchachenko's results for *N*-phenyl-2-naphthyl nitroxide are surprising. The nitroxide was made by heating H_2O_2 and the amine together with a trace of cobalt salt to 50–80° in an unspecified hydrocarbon solvent and then cooling the solution and recording the spectrum.[9b] Our results would indicate that a doublet splitting of ~4.0 G from the α-naphthyl proton ought to be readily resolvable. Thus, the possibility that Buchachenko's spectra partly involve radicals from these oxidative dimers must be considered. A complete answer to this question will have to entail unambiguous syntheses of *N*-phenyl-1- and *N*-phenyl-2-naphthyl nitroxides in larger amounts than heretofore possible.

Registry No.—**1b** (R = *p*-OCH_3), 27067-21-6; **1b** (R = *p*-CH_3), 27067-22-7; **1b** (R = *m*-CH_3), 27067-23-8; **1b** (R = H), 27067-24-9; **1b** (R = *m*-OCH_3), 27067-25-0; **1b** (R = *m*-Cl), 27067-26-1; **2b,** 27067-27-2; **3b,** 27067-28-3; **4b,** 27067-24-9; III, 27067-30-7; IV, 27067-31-8; V, 27067-32-9.

Acknowledgment.—The authors are grateful to O. M. Epifanio for technical assistance in measuring the spectra.

Restricted Rotation of Aryl Rings in *cis*-1,2-Diarylcyclopentanes and Diarylmethylcyclobutanes[1,2]

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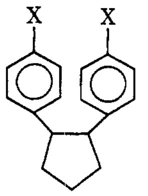
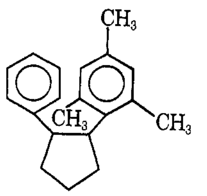
cis-1-Mesityl-2-phenylcyclopentane (*cis*-I) has been found to undergo rotation of the mesityl ring slowly enough to permit detection by a change in nmr line shape at low temperatures. At the coalescence temperature (−44°), the rate of rotation is approximately 160 sec^{-1}. Cyclobutylmesitylphenylmethane (IX), 3-bromomesitylcyclobutylphenylmethane (X), isopropylmesitylphenylmethane (XI), and β,β'-dimesityladipic acid (XIII) and its ester XII show restriction of rotation of the mesityl rings at room temperature or below; results of the studies of these compounds are compared with related examples which have been described previously. In the course of the synthetic work it has been found that, although cyclobutyldiphenylcarbinol and cyclobutyl(2,4-dimethylphenyl)phenylcarbinol (V) undergo dehydration with ring expansion on treatment with hot formic acid, cyclobutylmesitylphenylcarbinol (II), 9-anthrylcyclobutylphenylcarbinol (XIV), and cyclobutyl(2,3-dimethyl-9-anthryl)phenylcarbinol undergo dehydration under the same conditions without skeletal rearrangement. All of these dehydrations occur without skeletal rearrangement when the reaction is catalyzed by iodine. Mesitylphenylmethylenecyclobutane (IV) can be converted to 1-mesityl-2-phenylcyclopentene by treatment with hot trifluoroacetic acid.

In a search for isomerism due to restriction of rotation of adjacent aromatic rings, several *cis*-1,2-di(*p*-substituted phenyl)cyclopentanes (A) were previously investigated.[4] Nmr studies showed that the phenyl rings in such compounds rotate rapidly on the nmr time scale at room temperature around the single bonds joining them to the cyclopentane ring. The objective of the present work was to decrease the rate of rotation by placing substituents on the phenyl rings in such a way as to increase the energy barrier to rotation.



A



cis-I

The preparation of *cis*-1-mesityl-2-phenylcyclopentane was undertaken as a point of departure. A possible synthetic route seemed to be through cyclobutylmesitylphenylcarbinol (II). It was anticipated that conversion of carbinol II to olefin III would occur with the desired carbon skeletal rearrangement, since the analogous cyclobutyldiphenylcarbinol had been reported[5] to undergo such a Wagner–Meerwein rearrangement when treated with hot formic acid. Instead, the reaction of carbinol II with formic acid under the conditions reported previously for the diphenylcarbinol gave only the unrearranged methylenecyclobutane IV. The structure of IV was established by a comparison of its nmr, uv, and ir spectra with those of related compounds and by oxidation to mesityl phenyl ketone. This difference in behavior led to a reinvestigation of the dehydration reactions of the parent cyclobutyldiphenylcarbinol to be described later in this paper.

The conversion of the methylenecyclobutane IV to the desired cyclopentene III was accomplished by treatment with trifluoracetic acid. Catalytic hydrogenation of III gave the desired *cis*-cyclopentane *cis*-I. A similar series of reactions was employed to prepare the related 2,4-dimethylphenylcyclopentane *cis*-VII.

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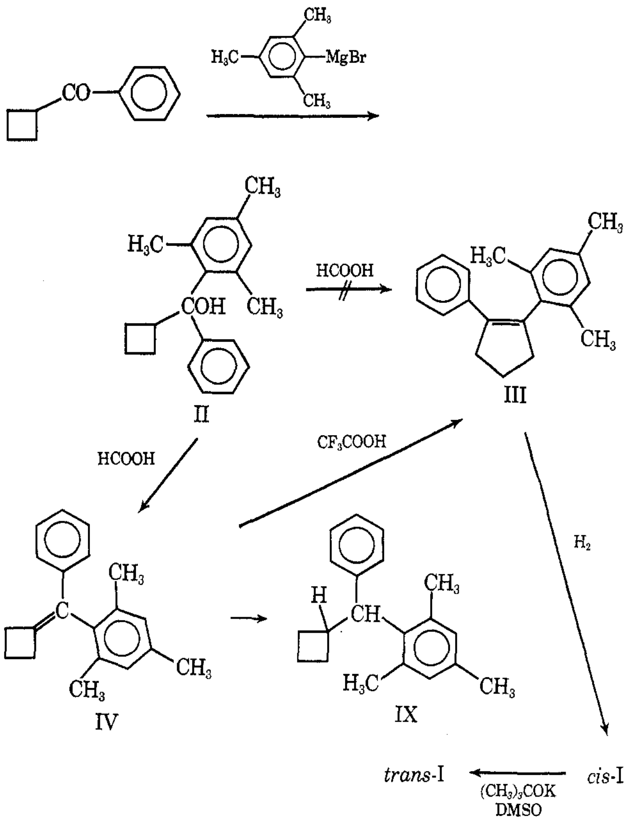
[1] Taken from the Ph.D. Theses, University of Illinois, of D. S. H. (1968) and P. E. B. (1969).

[2] We are indebted to the Army Research Office, Durham, and to the National Science Foundation for grants supporting this work.

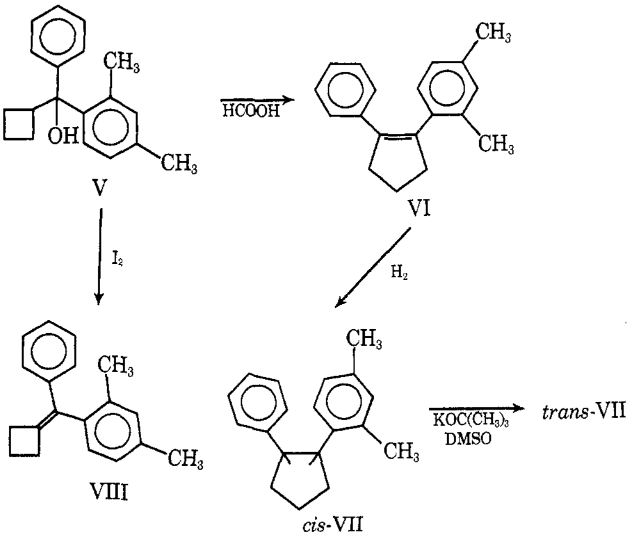
[3] U. S. Public Health Service Trainee, 1966–1969.

[4] D. Y. Curtin and S. Dayagi, *Can. J. Chem.*, **42**, 867 (1964).

[5] R. Criegee, A. Kerckow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955).



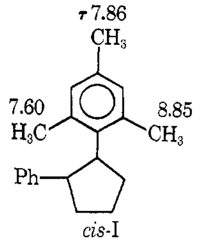
In this case the carbinol was converted directly by treatment with formic acid to the desired cyclopentene VI which was hydrogenated to the *cis*-cyclopentane *cis*-VII. Dehydration of the carbinol with iodine in benzene solution gave the corresponding methylene cyclobutane VIII. *cis*-Cyclopentanes I and VII could each be converted to its isomeric trans compound by treatment with potassium *tert*-butoxide in dimethyl sulfoxide.[6]



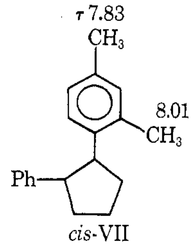
At room temperature the *cis*-mesitylphenylcyclopentane I showed an nmr spectrum indicative of rapid rotation of the mesityl group around the single bond to the cyclopentane ring. Thus, the absorption in carbon tetrachloride solution of the two *o*-methyl group protons occurred as a sharp singlet at τ 8.08 (with the para at τ 7.86). The broad benzylic proton absorption at τ 6.48 in *cis*-I was 0.1 ppm to lower field than the corresponding absorption of *trans*-I, a difference qualitatively similar to that between *cis*- and *trans*-1,2-diphenylcyclopentane and thus confirming the assigned configurations.[7] A similar difference was observed between *cis*- and *trans*-VII.

When the temperature of a solution of *cis*-I in carbon disulfide was lowered, the spectrum showed a broadening of the *o*-methyl absorption, and when −56° had been reached, the original peak had disappeared and two new peaks had become visible. At −81° fully developed sharp singlets of nearly equal intensity were seen at τ 7.6 and 8.9. (In carbon disulfide at room temperature the absorption resulting from coalescence is at τ 8.2, approximately equidistant from these two peaks.) The absorption of the *p*-methyl group was unchanged when the temperature was lowered. It seems clear that the nonequivalence of the *o*-methyl protons is due to the restriction of rotation of the mesityl ring so that at low temperatures the "inside" methyl group (more nearly over the cyclopentane ring) has a different chemical shift from the "outside" methyl group (away from the cyclopentane ring). This explanation is supported by the change in the mesityl ring proton spectrum at low temperatures. At room temperature *cis*-I showed a broad absorption due to the protons on the unsubstituted phenyl ring as was observed[7b] with *cis*-diphenylcyclopentane and, in addition, a sharp singlet at very slightly higher field (τ 3.49) due to the two meta ring protons of the mesityl group. At lower temperatures the mesityl ring proton absorption broadened, then disappeared, and at −62° a new doublet appeared, one arm of which, however, overlapped with the phenyl proton spectrum. The complexity of the spectra precludes an accurate calculation of the isomerization rate or even the coalescence temperature, but it seems clear that coalescence occurred near −44°; the method of Gutowsky and Holm[8] gives an estimated rate at that temperature of about 160 sec^{-1}. The assignment of this change in the nmr spectrum to restriction of the rotation of the mesityl ring was supported by the fact that no such change in the spectrum of the *cis*-VII was observed when it was cooled to −60°. The absence of even one of the *o*-methyl groups as in *cis*-VII would, of course, be expected to permit rotation of the dimethyl ring at a rate similar to that of the unmethylated compound *cis*-diphenylcyclopentane and its para-substituted derivatives previously studied.

The positions of the methyl group chemical shifts are summarized below, next to the formulas of *cis*-I and *cis*-VII. That in VII the *o*-methyl group's ab-



cis-I



cis-VII

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[6] See D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1963, p 32 ff.

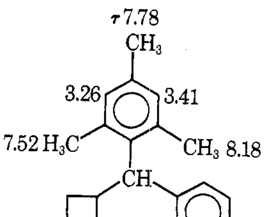
[7] (a) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (*London*), 1205 (1958); (b) D. Y. Curtin, H. Gruen, Y. G. Hendrickson and H. E. Knipmeyer, *J. Amer. Chem. Soc.*, **84**, 863 (1962).

[8] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1962).

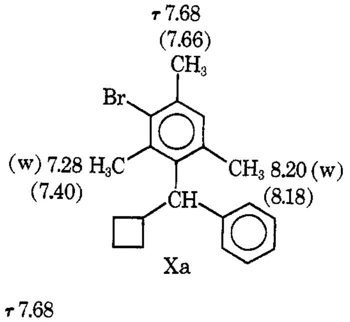
sorption position lies between the positions of the two *o*-methyl groups of *cis*-I is in agreement with the postulation that VII exists as a mixture of rapidly equilibrating conformers, one with the methyl group in the "inside" position and one "outside."

The temperature dependence of the nmr spectrum of cyclobutylmesitylphenylmethane (IX) prepared by hydrogenation of the methylenecyclobutane IV was also examined. At ambient temperature (38°) the mesityl ring proton absorption occurred as a singlet at τ 3.3, well separated from the phenyl proton singlet at τ 2.92. The *p*-methyl group on the mesityl ring appeared as a sharp singlet at τ 7.75; the *o*-methyl protons, however, gave rise to very broad absorption at the base of the *p*-methyl singlet and overlapping with the cyclobutane ring methylene proton absorption. At 0° the mesitylene ring protons had separated to a doublet at τ 3.26 and 3.41, and the *o*-methyl protons' absorption also had separated and sharpened so that the three methyl groups now appeared as singlets at τ 7.52, 7.78, and 8.18. In the case of this compound, as with *cis*-I, rotation of the mesityl group around its single bond is slow on the nmr time scale at low temperatures; the mesityl ring exists in a conformation such that its two sides have nonequivalent environments. The rate of rotation was estimated to be of the order of 100 sec^{-1} at the coalescence temperature of 38°. At 30°, the coalescence temperature of the mesityl ring proton absorption, the rate was calculated to be 20 sec^{-1} in reasonable agreement with the results from the *o*-methyl absorptions.

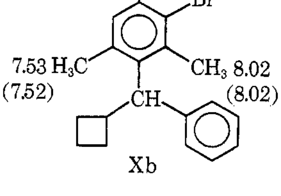
Bromination of the mesityl phenyl compound IX in acetic acid gave a monobromo compound shown by the nmr spectrum to have a single mesityl ring proton and therefore assigned the structure X. At ambient temperature the nmr spectrum resembled that of the unbrominated compound IX with a relatively sharp ring proton absorption but with broad *o*-methyl absorption. At 90° the *o*-methyl proton signals had sharpened so that there had appeared the three methyl absorptions expected if the mesityl ring is rotating rapidly. At −10° the spectrum of X was that to be expected from a mixture of two isomers in unequal amounts shown schematically and designated Xa and Xb without any attempt to describe their precise geometry. If the effect of a bromine atom on an *o*-methyl group is assumed to lower the absorption position 0.12 ppm,[9] and if the effect on a *p*-methyl absorption is assumed to be negligible, the positions of the methyl absorptions of Xa and Xb can be deduced from the methyl positions of the unbrominated compound IX with the further assumption that the bromine atom does not effect the position of the rotational equilibrium. The values so calculated are shown in parentheses beside the formulas together with the values observed in the spectrum of X. The absorptions at τ 7.28 and 8.20 were less intense than those at τ 7.53 and 8.02; an estimate of the relative intensities of the τ 7.28 and 7.53 absorptions led to an estimate of the ratio Xa/Xb as 1:2. The internal consistency of the chemical shift values provides support for the interpretation presented here.



IX

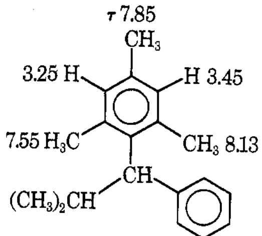


Xa

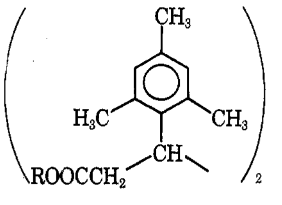


Xb

To determine the extent to which the barrier to rotation of the mesityl ring of *cis*-VII was a result of the presence of the cyclobutane ring, the related compound, isopropylmesitylphenylmethane (XI), with an isopropyl substituted for the cyclobutyl group, was prepared and the nmr spectrum determined. At ambient temperature the mesityl methyl proton absorption was a sharp singlet, as was the mesityl ring proton absorption. At lower temperatures (carbon disulfide solvent) the *o*-methyl proton absorption broadened, as did the absorption due to the mesityl ring protons, and at −52° the mesityl methyl group absorption appeared as three sharp well-separated peaks and the mesityl ring proton absorption appeared as a pair of sharp peaks. Chemical shift positions are shown on the accompanying formula. Using the method of Gutowsky and Holm,[8] the rate constant for rotation of the mesityl ring was estimated to be 78 sec^{-1} at the coalescence temperature of −4° for the methyl proton absorption and 28 sec^{-1} at the coalescence temperature of 16° for the mesityl ring proton absorption.



XI



XII, R = CH_3
XIII, R = H

A further example of nonequivalence of *o*-methyl groups on a mesityl ring was provided by examination of the nmr spectrum of dimethyl *meso*-β,β'-dimesityladipate (XII), which was prepared by electrolytic reduction[10] of 2,4,6-trimethylcinnamic acid followed by esterification with methanol and hydrochloric acid. Although the nmr spectrum of the ester XII showed the mesityl ring protons as a singlet at τ 3.16, the methyl groups of the mesityl ring were clearly separated from each other, the *p*-methyl group absorption appearing at τ 7.70 and the *o*-methyl group absorption at τ 7.32 and 7.40 (relative areas indicated that the latter two peaks which were not completely resolved from each

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(9) R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).

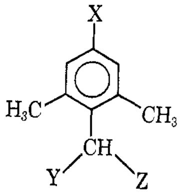
(10) We are very much indebted to Professor Sherlock Swann for helpful advice concerning this part of the work.

other, obscured the four methylene carbon protons). The corresponding carboxylic acid, β,β′-dimesityladipic acid (XIII), showed a mesityl ring spectrum like that of the ester.

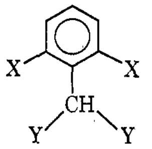
Compounds IX–XIII have in common restriction of rotation of a 2,6-dimethylphenyl ring around a single bond joining it to a tetrahedral carbon atom having two additional substituents. Related examples of such restriction of rotation have been reported recently[11–14] and are presented in Table I together with a summary of our results.

TABLE I

COALESCENCE TEMPERATURE (T_c) AND FREE ENERGIES OF ACTIVATION FOR 2,6-DISUBSTITUTED ARYL RINGS



B



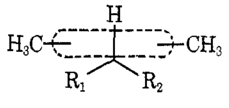
C

Structure	T_c, °C	$\Delta G^{\ddagger}$ at T_c (kcal/mol)	$\Delta\nu$, $ArCH_3$, ppm
Mesityldiphenylmethane[a,b] (B1, $X = CH_3$; $Y = Z = C_6H_5$)	−90[c]	8.8	
Mesitylisopropylphenylmethane[b,d] (XI) (B2, $X = CH_3$; $Y = (CH_3)_2CH$; $Z = C_6H_5$)	−4[c] (−16)[e]	13	0.58
Mesitylcyclobutylphenylmethane (IX)[b,d] (B3, $X = CH_3$; $Y = C_4H_7$; $Z = C_6H_5$)	38[c] (30)[e]	16	0.66
Dimethyl *meso*-β,β′-dimesityladipate (XII)[d,f] (B4, $X = CH_3$; $Y = CH(CH_2COOCH_3)C_6H_2$-$(CH_3)_3$-2,4,6; $Z = CH_2COOCH_3$)	>30[c]		0.08
β,β′-Dimesityladipic acid (XIII)[d,g] (B5, $X = CH_3$; $Y = CH$-$(CH_2COOH)C_6H_2(CH_3)_3$-2,4,6; $Z = CH_2COOH$)	>30		0.06
1,2-Dimethyl-1,2-bis(2,6-dimethylphenyl)ethanes[h,i] (B6, $X = H$; $Y = CH_3$; $Z = CH(CH_3)$ $C_6H_3(CH_3)_2$-2,6)			
meso	104[c]	24	0.14
dl	171[c]	19	0.80
9-Mesitylfluorene[j] (B7, $X = CH_3$; $Y, Z = -C_6H_4C_6H_4-$)	>200[f]	≥26	1.54
Tri(2,6-dimethoxyphenyl)methane[a] (C1, $X = CH_3O$; $Y = Z = C_6H_2(OCH_3)_2$-2,6)	−57[b]	11	
2,6-Dichlorobenzal chloride[k] (C2, $X = Y = Cl$)	25[e]	15	

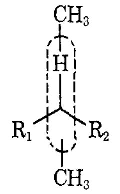
[a] Reference 11. [b] Solvent CS_2. [c] Coalescence of the methyl proton spectrum. [d] Present results. [e] Coalescence of the ring spectrum protons. [f] Solvent $CDCl_3$. [g] Solvent dimethyl sulfoxide. [h] Reference 12. [i] Solvent C_6H_5Cl. [j] Reference 14. [k] Reference 13.

The compound in Table I with structure B which has the lowest coalescence temperature and barrier to rotation is mesityldiphenylmethane, in which groups X and Y are phenyl rings. Replacement of one phenyl ring with an isopropyl group (structure XI) increases the interference to rotation of the mesityl ring, and replacement with a cyclobutyl group as in IX increases the interference even more. Substitution of much bulkier groups, as is found in the compounds further along in Table I, leads to increasing barriers to rotation. It is particularly striking that the compound B7, with the largest barrier to rotation of the mesityl ring (9-mesitylfluorene), differs from the compound B1 with the smallest barrier (mesityldiphenylmethane) only by virtue of having the two phenyl rings joined together by an extra bond. A difference of this kind was qualitatively anticipated by Adams and Campbell[15] and by Siddal and Stewart[14] on the basis that synchronous rotation possible in the diphenyl compound is prevented by the joining of the rings in the fluorenyl molecule. Such a "cogwheel effect" has been invoked in other systems by Kwart and Alekman[16] and may be partially responsible for the difference between the rate of rotation of the mesityl ring in the isopropyl compound XI as compared with the cyclobutyl compound IX in the present work.

In previous considerations[11,12,14] of the conformations of minimum energy associated with rotation of the mesityl group of molecules of type B (Table I), two states have been given particular attention. In one (D), viewed along the bond joining the tetrahedral carbon atom to the mesityl ring, the mesityl methyl groups lie between R_1 or R_2 and the hydrogen atom. In the other (E), one methyl lies between R_1 and R_2, with the other in a position more or less opposed to the hydrogen atom. In each case (B1, B6, and B7 of Table I) the conformation E has been chosen[11,12,14] as the one of minimum energy, and it seems likely that the same considerations apply to the compounds examined in the present work (B2, B3, B4, and B5 of Table I). The difference in magnetic environment of the two methyl groups of the mesityl ring under condition in which rotation is slow on the nmr time scale is given by the chemical shift difference in Table I. Evidence that the dimesityl adipate XII has the meso configuration is provided by the similarity of the Δν (0.08 ppm) to that of the *meso*- but not the *dl*-dimesityldimethylethane B5 (Table I). The reason for the difference between *meso*- and *dl*-B6 has been discussed.[12]



D



E

Dehydration of Diarylcyclobutylcarbinols.—Our observation that formic acid dehydration of cyclobutylmesitylphenylcarbinol II produced dehydration without carbon skeleton rearrangement, in contrast to the reported[5] behavior of the related compound, cyclobutyldiphenylcarbinol, led to a reinvestigation of the latter reaction. The literature was somewhat con-

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(11) H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

(12) A. J. M. Reubers, A. Sinnema, F. van Rantwijk, J. D. Remijnse, and H. van Bekkum, *ibid.*, **25**, 4455 (1969).

(13) T. Schaefer, R. Schwenk, C. J. McDonald, and W. F. Reynolds, *Can. J. Chem.*, **46**, 2187 (1968).

(14) T. H. Siddall, III, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969).

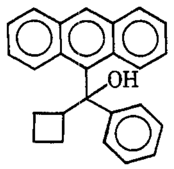
(15) R. Adams and J. Campbell, *J. Amer. Chem. Soc.*, **72**, 153 (1950).

(16) H. Kwart and S. Alekman, *ibid.*, **90**, 4482 (1968).

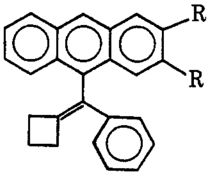
fusing with regard to this dehydration. Kishner[17] first reported that the dehydration of cyclobutyldiphenylcarbinol with oxalic acid dihydrate gave diphenylmethylenecyclobutane without carbon skeleton rearrangement. This work was not mentioned in the report of the dehydration with carbon skeleton rearrangement by formic acid by Criegee, Kerckow, and Zinke,[5] which in turn was not referred to in a later report by Graham and Williams[18] that either iodine in benzene or oxalic acid dihydrate gave only unrearranged diphenylmethylenecyclobutane. Because of the coincidental agreement of many of the properties of diphenylmethylenecyclobutane with those of 1,2-diphenylcyclopentene (see the Experimental Section), these dehydrations were reinvestigated. The report of Graham and Williams[18] that dehydration of the diphenylcarbinol with iodine proceeded without rearrangement and that of Criegee that reaction with formic acid gave only rearranged product were both confirmed. However, oxalic acid dihydrate was found to give a nearly equimolar mixture of rearranged and unrearranged olefin, in contrast to the report of Graham and Williams.[18]

It deserves mention that infrared and ultraviolet spectroscopy, unlike the nmr and mass spectra, provided easy differentiation between the diarylmethylene cyclobutanes and the 1,2-diarylcyclopentenes. Diphenylmethylenecyclobutane and its methyl derivatives IV and VIII showed absorption at 2983 ± 3, 2918 ± 3, 2824 ± 4, and 1414 ± 1 cm^{-1}. The diarlycyclopentenes (1,2-diphenylcyclopentene, III, and VI) showed none of these absorptions and instead had characteristic absorptions at 2891 ± 1, 2868 ± 3, and 2843 ± 3 cm^{-1}. The diarylmethylenecyclobutanes showed their longer wavelength absorption maxima in the ultraviolet spectrum at 260 cm^{-1} or less, whereas the corresponding absorption in the diarylcyclopentenes was at a longer wavelength than 260 nm; with a particular pair of aryl groups the absorption of the diarylcyclopentene was 16–20 nm higher in wavelength than that of the corresponding diarylmethylenecyclobutane.

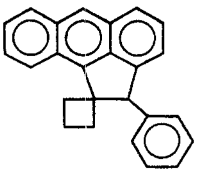
In an effort to increase dramatically the steric interference to rotation in this *cis*-1,2-diarylcyclopentane systems, cyclobutyl(9-anthryl)phenylcarbinol (XIV) was prepared from 9-anthryllithium and phenylcyclobutyl ketone. The structure was confirmed by the infrared spectrum which showed the absorptions characteristic of the methylene cyclobutane system. Dehydration with either iodine–benzene or with formic acid gave only the methylenecyclobutane (XV). The related olefin XVI was prepared from 2,3-dimethyl-9-anthryllithium in a similar manner. An attempt to cause rearrangement of the methylenecyclobutane XV to the corresponding anthrylphenylcyclopentene failed, and instead there was obtained a product believed to have resulted from a Friedel–Crafts ring closure and to be XVIIa or XVIIb.



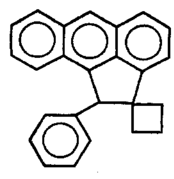
XIV



XV, R = H
XVI, R = CH_3



XVIIa



XVIIb

It follows that dehydration of cyclobutyldiarylcarbinols when carried out with hot formic acid leads to rearrangement to the diarylcyclopentene when both aryl groups are relatively unhindered as with cyclobutyldiphenylcarbinol or with the 2,4-dimethylphenyl compound V. The demonstration that the compounds II and XIV were dehydrated with no observable rearrangement suggests that steric factors are responsible for the difference in behavior.

Experimental Section[19]

Cyclobutylmesitylphenylcarbinol (II).—To a solution of mesitylmagnesium bromide prepared from 52 g (0.25 mol) of bromomesitylene[20] and 7 g (0.29 g-atom) of magnesium turnings in 250 ml of tetrahydrofuran (THF) freshly distilled from $LiAlH_4$ was added 40 g (0.25 mol) of cyclobutylphenyl ketone in 100 ml of dry THF over a 10-min period. After the mixture was stirred for 4.5 hr, decomposition by pouring into 1 l. of cold saturated NH_4Cl solution and extraction with ether gave on distillation a fraction with bp 110–175° (0.5 mm). Redistillation gave a viscous yellow oil which crystallized on standing. Recrystallization from pentane yielded 14.7 g (21%) of carbinol II, mp 89–91°. Recrystallization gave product, mp 91–92°. The infrared spectrum showed absorption at 3605 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}O$: C, 85.7; H, 8.6. Found: C, 85.4; H, 8.6.

Mesitylphenylmethylenecyclobutane (IV). A. Dehydration with Formic Acid.—The carbinol II (10 g, 3.6 mmol) in 400 ml of 98% formic acid was heated for 10 hr with stirring under reflux. After dilution with water, extraction with chloroform, washing with aqueous $NaHCO_3$, drying of the chloroform solution, and distillation, there was obtained 8.15 g (90% yield) of a clear oil, bp 138–145° (0.4 mm), which crystallized on standing. Recrystallization from ethanol gave the methylenecyclobutane IV: mp 47–48°; uv max 255 nm (ϵ 17,350, sh), 262 (18,100), 272 (12,300, sh); ir 2980, 2910, 2820 (w), 1650 (w), 1412 cm^{-1}; nmr τ 2.96 (s, 5), 3.26 (s, 2), 6.87 (t, 2), 7.60 (m, 2), 7.76 (s, 4), 7.96 (s, 7).

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[17] N. Kishner, *J. Russ. Phys. Chem. Soc.*, **42**, 1288 (1910).

[18] S. H. Graham and A. J. S. Williams, *J. Chem. Soc.*, 4066 (1959); *ibid.*, *C*, 655 (1966); 390 (1969).

[19] The more important spectra are reproduced in the two dissertations available from University Microfilms, Ann Arbor, Mich. Mesitylphenylmethylenecyclobutane (IV), its reduction product (IX), and the bromo derivative (X) of IX, first described in the thesis[1] of D. S. H., are there incorrectly referred to as the cyclopentene III, the cyclopentane *cis*-I, and the bromo derivative of *cis*-I, respectively. Similarly, the anthrylphenylmethylenecyclobutanes XV and XVI are there incorrectly identified as 1-anthryl-2-phenylcyclopentenes.

Melting points were determined on a Kofler hot stage or a Thomas-Hoover apparatus and are corrected. Ultraviolet spectra were obtained with a Spectronic 505 or a Cary Model 14 spectrophotometer; hexane solutions were used unless otherwise indicated. Infrared spectra (10–20% solutions in carbon tetrachloride unless otherwise indicated) were measured in part by Mr. D. Johnson and his associates and were obtained with a Perkin-Elmer Model 21 or 521 spectrophotometer. Nmr spectra were determined in part by Mr. R. Thrift, Mr. O. Norton, and Mr. D. Johnson and their associates with Varian Model A-60, A-60A, 56-60A, or HA-100 instruments (CCl_4 unless otherwise specified), with tetramethylsilane as in internal standard. Solutions (5–30%) employed in the temperature dependence studies were degassed. Mass spectra (70 eV) were obtained with an Atlas CH-4 spectrometer by Mr. J. Wrona. Microanalyses were determined by Mr. J. Nemeth and his associates.

[20] L. I. Smith, "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, p 45.

Anal. Calcd for $C_{20}H_{22}$: C, 91.6; H, 8.5. Found: C, 91.3; H, 8.4.

B. Dehydration with Iodine.—When the carbinol II (2.5 g, 8.9 mmol) in 60 ml in benzene with 0.1 g of iodine was heated under reflux for 16 hr and the solution washed with aqueous sodium thiosulfate and then water, dried, heated with Darco, filtered through a Celite pad, and distilled, there was obtained 1.85 g (80% yield) of the methylenecyclobutane IV as an oil which crystallized on standing, mp 46.2–47.8°. A mixture with the product obtained by the dehydration with formic acid showed no melting point depression.

Oxidation of Mesitylphenylmethylenecyclobutane (IV).—Treatment of 400 mg (1.53 mmol) of olefin IV in 120 ml of *tert*-butyl alcohol with 1.68 g (7.85 mol) of sodium periodate, 0.31 g (1.96 mmol) of potassium permanganate, 0.28 g (2.03 mmol) of potassium carbonate, and 250 ml of water for 64 hr[21] gave, after dilution with water, extraction with ether, drying of the ether solution, and removal of the ether on a rotary evaporator, 191 mg of an oil whose behavior on thin layer chromatography (benzene, silica gel G) showed a major component with a R_f like that of mesitophenone. Column chromatography on alumina (ligroin:benzene, 1:1, as eluent) of the original reaction product gave a fraction with the nmr spectrum characteristic of mesitophenone: τ 2.26 (m, 2), 2.66 (m, 3), 3.20 (s, 2), 7.26 (m, 1), 7.70 (s, 3), 7.96 (s, 6). The ir spectrum contained every band present in the spectrum of authentic mesitophenone.

1-Mesityl-2-phenylcyclopentene (III). Isomerization of IV with Trifluoroacetic Acid.—A solution of 3.0 g (11.4 mmol) of the methylenecyclobutane IV in the minimum amount of carbon tetrachloride was heated under reflux for 12 hr with 50 ml of trifluoroacetic acid. After it was poured into ice water, the product was isolated by extraction with chloroform, washing with cold, saturated sodium carbonate solution, drying, removal of the solvent with a rotary evaporator, and chromatography on silica gel (petroleum ether eluent). There was obtained 28 g (93%) of III as a colorless oil. Tlc on silica gel G (petroleum ether) showed evidence of only one component as did glc (15% FFAP on Chromosorb G, 180°). Collection of this material gave an analytical sample: ir absorption at 3090, 3060, 3030, 2945, 2920, 2890 sh, 2865, 2840, 2725, 1610, 1595, 1495, 1442, 1375, 1030, 845, 690 cm^{-1}; nmr τ 3.00 (s, 5), 3.25 (s, 2), 6.8–7.6 (m, 4), 7.74 (s, 3, *p*-CH_3), 7.93 (s superimposed on a multiplet with total area 8); uv max 263 nm (ϵ 16,300).

Anal. Calcd for $C_{20}H_{22}$: C, 91.6; H, 8.5. Found: C, 91.8; H, 8.6.

cis-**1-Mesityl-2-phenylcyclopentane** (*cis*-**I**).—Reduction of the olefin III (2.8 g, 10.7 mmol) in 50 ml of absolute ethanol was carried out with hydrogen at 800 psi for 96 hr with 1.0 g of Pd on carbon as catalyst. After filtration through a Celite pad, removal of the solvent with a rotary evaporator, and recrystallization from absolute ethanol, there was obtained 1.9 g (67%) of *cis*-I as colorless prisms: mp 57.5–58.6°; further recrystallization gave mp 58.3–58.9.°; uv max 268 nm (ϵ 355), 262 (379); ir 3085, 2950, 1600 cm^{-1}; nmr (CCl_4) τ 3.05 (m, 3), 3.30 (s, 2), 3.49 (s, 2), 6.48 (m, 2), 7.86 (s), 8.08 (s) (the last two superimposed upon a multiplet, total area 15); mass spectrum (rel intensity) *m/e* 264 (81), 173 (18), 159 (51), 147 (27), 145 (45), 144 (75), 133 (100), 129 (37), 91 (24).

Anal. Calcd for $C_{20}H_{24}$: C, 90.9; H, 9.2. Found: C, 90.9; H, 9.3.

trans-**1-Mesityl-2-phenylcyclopentane** (*trans*-**I**).—The isomerization of *cis*-I (1.5 g, 5.67 mmol) was carried out by heating it for 12 hr at 100° under nitrogen with 3.0 g (26.7 mmol) of potassium *tert*-butoxide in 150 ml of dry dimethyl sulfoxide. The reaction mixture was then poured into 600 ml of ice water and extracted with petroleum ether, and the solvent evaporated. The brown oil so obtained (1.06 g, 63% yield estimated from the nmr spectrum) was distilled and submitted to glc. Collection of the major component (Apiezon L on Chromosorb W) gave *trans*-I: uv max 271 (ϵ 493), 267 (464), 264 (499), 262 (491); ir 3080, 2955, 1600, 1450 cm^{-1}; nmr τ 2.99 (s, 5), 3.38 (s, 2), 6.58 (m, 2), 7.85 (s), 7.88 (s) (the last two singlets superimposed on a multiplet, the total areas being 15).

Anal. Calc for $C_{20}H_{24}$: C, 90.9; H, 9.2. Found: C, 90.6; H, 9.1.

Cyclobutyl(2,4-dimethylphenyl)phenylcarbinol (V) was prepared by the addition of 20.3 g (0.127 mol) of cyclobutyl phenyl ketone to the Grignard reagent from 23.5 g (0.127 mol) of 2,4-dimethylbromobenzene and 3.2 g (0.132 g-atom) of Mg turnings in 200 ml of dry THF. After 10 hr under reflux, the reaction mixture was treated with cold saturated NH_4Cl solution, and the product isolated by extraction with ether and distillation to give 20 g (58%) of V as a clear oil, bp 145–146° (0.16 mm), which crystallized on standing. Recrystallization from pentane gave carbinol V: mp 66.0–66.5°; ir 3605 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}O$: C, 85.7; H, 8.3. Found: C, 85.4; H, 8.3.

1-(2,4-Dimethylphenyl)-2-phenylcyclopentene (VI) was formed when 20 g (0.075 mol) of carbinol V was heated under reflux in 500 ml of 98% formic acid for 11 hr. After dilution with water, extraction with chloroform, washing with saturated $NaHCO_3$ solution, and drying, distillation under vacuum gave 17 g (91%) of VI as a clear, viscous liquid: bp 130° (0.25 mm); n^{25}_{D} 1.5980; uv max 265 nm (ϵ 15,750); ir 1445, 700 cm^{-1}; nmr τ 3.0 (s, 5), 3.10 (s, 3), 7.25 (m, 4), 7.76 (s, 3), 8.03 (s, superimposed on multiplet, total area 5).

Anal. Calcd for $C_{19}H_{20}$: C, 91.9; H, 8.1. Found: C, 91.8; H, 8.1.

Oxidation of 1-(2,4-Dimethylphenyl)-2-phenylcyclopentene (VI). 1-(2,4-Dimethylphenyl)-5-phenylpentane-1,5-dione.—Potassium permanganate (28 ml of 0.4% aqueous solution) was added dropwise over 40 hr to 0.5 g of cyclopentene VI, 2.89 g of sodium metaperiodate, 0.48 g of potassium carbonate, and 5 ml of water in 60 ml of *tert*-butyl alcohol. Dilution with water, extraction with ether, and removal of the ether left an oil which was subjected to vpc (5-ft column, 265°). In addition to 34% of recovered starting material and 25% of an unidentified fraction, there was obtained 41% of the dione (as a third fraction), a yellow oil which crystallized from ethanol. The dione had mp 72–73°; ir 1680, 1480, 1240, 885, 685 cm^{-1}; nmr τ 2.1 (m, 2), 2.6 (m, 3), 3.1 (m, 2), 7.1 (m, 4), 7.7–8.2 (multiplet punctuated by two sharp peaks, 8).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2. Found: C, 81.1; H, 7.4.

cis-**1-(2,4-Dimethylphenyl)-2-phenylcyclopentane** (*cis*-**VII**).—Hydrogenation of the olefin (8.0 g, 0.032 mol) in 250 ml of ethanol was carried out for 6 hr at room temperature in the presence of 1.0 g of 5% Pd on carbon with a H_2 pressure of 300 psi. After filtration through a Celite pad and removal of the solvent under vacuum, distillation gave 6 g (74%) of clear oil, bp 154–157° (1.3 mm), which crystallized on cooling. Recrystallization from ethanol gave *cis*-VII (40% yield) as white needles: mp 63–63.5°; uv max 279 nm (ϵ 418), 270 (528), 262 (469); ir 3080, 1600, 1452 cm^{-1}; nmr τ 3.08 (m, 3), 3.37 (m, 5), 6.57 (m, 2), 7.83 (s), 8.01 (s), the last two peaks superimposed on a multiplet (total area 12); mass spectrum (rel intensity) *m/e* 250 (100), 159 (92), 146 (23), 145 (66), 144 (28), 133 (28), 132 (51), 131 (64), 129 (31), 120 (23), 119 (75), 117 (49), 115 (35), 106 (34), 105 (23), 91 (54).

Anal. Calcd for $C_{19}H_{22}$: C, 91.1; H, 8.9. Found: C, 90.9; H, 8.8.

(2,4-Dimethylphenyl)phenylmethylenecyclobutane (VIII).—Dehydration of 8.0 g (0.03 mol) of carbinol V with 0.2 g (0.8 mmol) of iodine in 300 ml of benzene was accomplished by heating under reflux (argon atmosphere) for 7 hr in apparatus equipped with a Dean–Stark water separator. After removal of the iodine by extraction with aqueous sodium thiosulfate, washing with water, drying, and removal of the solvent under vacuum, there resulted an orange oil which after two crystallizations from ethanol gave 6.1 g (82%) of the cyclobutane VIII: mp 39.2–40.0°; ir 3084, 3058, 3020, 2980, 2952, 2920, 2864, 2820, 1655 (w), 1415 cm^{-1}; uv max 272 nm (ϵ 12,400, sh), 261 (18,600), 257 (18,400), 247 (15,500), sh).

Anal. Calcd for $C_{19}H_{20}$: C, 91.9; H, 8.1. Found: C, 92.0; H, 8.2.

trans-**1-(2,4-Dimethylphenyl)-2-phenylcyclopentane** (*trans*-**VII**).—Isomerization of *cis*-VII (0.51 g, 2.04 mol) was carried out by heating it for 12 hr at 95–100° under argon with a solution of 1.05 g (9.38 mmol) of potassium *tert*-butoxide in 35 ml of dry dimethyl sulfoxide. The solution was poured into water and extracted with benzene, and *trans*-VII was separated by chromatography on silica gel (ligroin eluent) of the oil remaining after distillation of the benzene. Analysis by glc (Chromosorb W-Apiezon L, 252°) showed only two peaks corresponding to the starting material and a single product. Distillation at 0.1 mm gave *trans*-VII as a colorless oil: uv max 279 nm (ϵ 528), 271 (681), 264 (573); ir 3080, 2950, 1600, 1450 cm^{-1}; nmr τ 2.82–3.29 (m, 8), 6.86 (m, 2), 7.80 (s), 8.08 (s), the last two sin-

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(21) E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

glets superimposed on broad absorption, the total area being 12.

Anal. Calcd for $C_{19}H_{22}$: C, 91.1; H, 8.9. Found: C, 90.7; H, 8.8.

Cyclobutylmesitylphenylmethane (IX) was prepared by hydrogenation of 11.5 g (4.4 mmol) of the methylenecyclobutene IV in 250 ml of absolute ethanol over 1 g of 5% Pd on carbon for 24 hr at 300 psi. After filtration through a Celite pad and removal of the solvent, there was formed a clear oil which slowly crystallized. Recrystallization from ethanol gave 9.8 g (83%) of IX as white needles: mp 57.5–58°; uv max 245 (ϵ 370), 253 (490), 264 (581), 271 (535), 276 (280), 280 (185); ir 1445, 850, 710, 690 cm^{-1}; nmr 2.92 (s, 5), 3.30 (s, 2), 5.45 (d, 1, J = 9.9 Hz), 6.16 (m, 1), 7.25–8.6 (broadened multiplet with a sharp singlet at τ 7.7, total area 15); mass spectrum (rel intensity) *m/e* 264 (31), 209 (100), 165.5 (ms).

Anal. Calcd for $C_{20}H_{24}$: C, 90.9; H, 9.2. Found: C, 90.7; H, 9.4.

Bromomesitylcyclobutylphenylmethane (X) was prepared by treatment of 2.0 g (7.6 mmol) of hydrocarbon IX with 0.5 ml (9 mmol) of bromine in 75 ml of glacial acetic acid for 6 hr in the dark at ambient temperature. Addition of water, extraction with ether, washing with saturated Na_2CO_3 solution, drying over $MgSO_4$, and distillation of the ether left a clear oil which crystallized from ethanol to give 2.4 g (89%) of X as fine white needles: mp 73°; nmr 2.95 (d, 5), 3.16 (s, 1), 5.42 (d, 1), 6.75 (m, 1), 7.1–8.6 (broad multiplet punctuated by a sharp singlet at 7.68, total area 15); mass spectrum (rel intensity) *m/e* 344 (32), 342 (32), 289 (100), 287 (100), 243 (ms), 241 (ms).

Anal. Calcd for $C_{20}H_{23}Br$: C, 70.0; H, 6.8; Br, 23.3. Found: C, 69.8; H, 6.6; Br, 23.3.

1-Mesityl-1-phenyl-2,2-dimethylethylene.—To mesitylmagnesium bromide prepared from 30.0 g (0.15 mol) of mesityl bromide and 4.1 g (0.17 g-atom) of magnesium turnings in 350 ml of dry tetrahydrofuran was added 18.2 g (0.12 mol) of isobutyrophenone. After 15 hr under reflux, the solution was acidified with cold saturated aqueous ammonium chloride and extracted with ether, the ether solution separated and dried, the ether removed on a rotary evaporator, and the residue distilled to give a yellow oil, bp 131.5–154° (0.12 mm). Chromatography on silica gel (elution with benzene–petroleum ether) followed by recrystallization from absolute ethanol gave 2.2 g (7.1%) of the desired diarylethylene as colorless prisms: mp 61–62°; uv max 242.5 (ϵ 13,500); ir 1610 cm^{-1} (C═C); nmr τ 2.94 (s, 5), 3.26 (s, 2), 7.79 (s, 3), 7.91 (s, 6), 8.04 (s, 3), 8.47 (s, 3).

Anal. Calcd for $C_{19}H_{22}$: C, 91.1; H, 8.9. Found: C, 91.3; H, 9.0.

Isopropylmesitylphenylmethane (XI).—Hydrogenation of 1-mesityl-1-phenyl-2,2-dimethylethylene (2.07 g, 8.7 mmol) in 80 ml of absolute ethanol was carried out for 160 hr at 600 psi over 1.0 g of 5% Pd on carbon at ambient temperature. After filtration through a Celite pad, removal of the solvent, and distillation, there was obtained 1.3 g (64%) of colorless oil, bp 98.5–100.5°. Preparative glc through a column packed with 20% Apiezon L on Chromosorb W (230°) removed two minor components and gave XI as the major fraction: ir no absorption at 1610 cm^{-1}; nmr τ 2.87 (s, 5), 3.35 (s, 2), 5.90 (d, 1, J = 10.5 Hz), 7.26 (m, 1), 7.81 (s, 9), 8.80 (d, 3, J = 6.5 Hz), 9.26 (d, 3, J = 6.5 Hz).

Anal. Calcd for $C_{19}H_{24}$: C, 90.4; H, 9.6. Found: C, 90.1, 89.9; H, 9.5, 9.5.

Dimethyl β,β'-Dimesityladipate (XII).—β,β'-Dimesityladipic acid[22] (25 g, 0.21 mol) was reduced in 300 ml of dimethylformamide containing 65 ml of 28% aqueous sulfuric acid at 20° at a mercury electrode with a current density of 0.03 A/cm^2 for 1.25 hr following a procedure analogous to that previously described[23] for the reduction of cinnamic acid.

The yellow catholyte, after decantation from the mercury, was poured into 1.5 l. of cold water, and the flocculent precipitate was filtered and washed with benzene and ether to leave a pasty white solid. Recrystallization from isopropyl alcohol gave 3.36 g (13.5%) of white crystals of acid (XIII): mp 297–299°; ir (KBr disk) 1710, 852 cm^{-1}; nmr (DMSO-d_6) τ 3.18 (s, 4), 5.76 (m, 2), 7.5 (d, broadened, 14), 7.83 (s, 5); nmr (pyridine) τ 5.20 (m, 2), 6.5–7.1 (m, 2), 7.21 (d, 15), 7.89 (s, 6); mass spectrum *m/e* 382.

Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.4; H, 7.9. Found: C, 74.5; H, 8.0.

The acid XIII (0.295 g, 0.785 mmol) was heated under reflux for 12 hr with 35 ml of anhydrous methanol saturated with HCl. Removal of the solvent under vacuum gave 0.205 (65%) of white needles, which after recrystallization from methanol gave XII: mp 140–141°; ir ($CHCl_3$) 1725, 1165, 855 cm^{-1}; nmr ($CDCl_3$) τ 3.16 (s, 4), 5.60 (m, 2), 6.70 (s, 6), 7.15 (m, 1), 7.45 (d, 15), 7.79 (s, 6).

Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.1; H, 8.4. Found: C, 75.7; H, 8.5.

Dehydration of Cyclobutyldiphenylcarbinol. A. With Iodine.—The reaction carried out according to the directions of Graham and Williams[18] gave a 76% yield of diphenylmethylenecyclobutane in agreement with their work. The physical properties of the product are reported in Table II to permit ready comparison with those of the isomeric substance 1,2-diphenylcyclopentene.

TABLE II

COMPARISON OF THE PHYSICAL AND SPECTRAL PROPERTIES OF DIPHENYLMETHYLENECYCLOBUTANE AND 1,2-DIPHENYLCYCLOPENTENE AND THEIR DERIVATIVES

Property obsd	Diphenylmethylenecyclobutane	1,2-Diphenylcyclopentane
Mp,[a] °C	57.0–57.5 (lit.[b] 57–58)	59.5–60.5 (lit.[b,c] 59, 62.5–63)
Uv, nm (ϵ)	max 257 (15,600) [lit.[d] max 257 (17,000)]	max 274 (11,300)
Ir	3085, 3060, 3028, 2985 2955, 2915, 2828 (w), 1650 (w), 1598, 1415 cm^{-1}	3085, 3060, 3028 (d), 2955, 2892 (sh), 2870, 2845, 1600 cm^{-1}
Nmr, τ	2.88 (s, 10), 7.10 (t, 4.0, J = 7.8 Hz), 8.01 (q, 2.0, J = 7.8 Hz)	2.93 (s, 10.3), 7.12 (t, 4.0, J = 7.3 Hz), 8.01 (q, 2.0, J = 7.3 Hz)
Mass spectrum (rel intensity), *m/e*	220 (100), 219 (20.2), 205, 53.9), 192 (46.6), 191 (56), 165 (20.2), 129 (32.6), 91 (20.7)	220 (100), 219 (24.8), 205 (14), 192 (6.2), 191 (8.8), 165 (4.6), 129 (16.8), 91 (16.4)
Mp of oxidation products, °C	48,[e] 87.5–89.5[f]	65–66[g]

[a] A 50:50 mixture of diphenylmethylenecyclobutane and 1,2-diphenylcyclopentene showed a 12° depression. [b] Reference 18. [c] Reference 5. [d] K. V. Scherer, Jr., and R. S. Lunt III, *J. Org. Chem.*, **26**, 5183 (1961). [e] Benzophenone, ref 7. [f] 2,2-Diphenylcyclopentanone: N. R. Easton and S. J. Nelson, *J. Amer. Chem. Soc.*, **75**, 640 (1953). [g] 1,5-Diphenylpentane-1,5-dione, ref 2, 3.

B. With Formic Acid.—Formic acid dehydration carried out following the directions of Criegee, Kerckow, and Zinke[5] gave 1,2-diphenylcyclopentene as reported by them. The physical and spectral properties are reported in Table II.

C. With Oxalic Acid.—Cyclobutyldiphenylcarbinol (4.0 g, 0.017 mol) which had been ground with 16 g (0.178 mol) of oxalic acid dihydrate was heated for 4 hr at 160° under argon in equipment which permitted distillation of volatile products. Addition of ether and extraction with dilute aqueous sodium hydroxide solution gave after evaporation of the ether an oil which solidified on standing. Since the component olefins were shown not to be readily separated by glc under the conditions attempted, the mixture was oxidized by the prodedure of von Rudloff;[24] 300 mg (1.4 mmol) of the olefin mixture was treated with 1.2 g (5.9 mmol) of sodium periodate, 0.23 g (1.4 mmol) of potassium permanganate, and 0.21 g (1.5 mmol) of potassium carbonate in 300 ml of 31% aqueous *tert*-butyl alcohol for 50 hr. After dilution with water, extraction with ether, and drying and evaporation of the ether, the mixture of oxidation products was analyzed with glc on a column of 10% SF-96 on Chromosorb W (268°). There was found to be 53% 1,5-diphenylpropane-1,3-dione and 47% benzophenone. When the same procedure was applied to a mixture of diphenylmethylenecyclobutane and 1,2-diphenylcyclopentene (1:1), the analysis gave 52% pentanedione and

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(22) N. Thomas and R. C. Fuson, *J. Org. Chem.*, **18**, 1762 (1953).

(23) C. L. Wilson and K. B. Wilson, *Trans. Electrochem. Soc.*, **84**, 153 (1943).

(24) E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

48% benzophenone. Oxidation of authentic diphenylmethylenecyclobutane and glc analysis by this procedure gave peaks with the retention time of benzophenone (2.97 min) and 1,5-diphenylpentane-1,5-dione (27 min) with areas which when standardized with known mixtures of the ketones showed the presence of 99.3% benzophenone and 0.7% diphenylpentanedione (seeding with benzophenone induced cyrstallization of the oily product) with a yield of 78%. A similar procedure applied to 1,2-diphenylcyclopentene gave a 48% yield of crystalline 1,5-diphenylpentane-1,5-dione, mp 65.2–66° (compare Table II), shown by glc to be free from benzophenone.

Preparation and Dehydration of Cyclobutyl(9-anthryl)phenyl carbinol (XIV). (9-Anthryl)phenylmethylenecyclobutane (XV). —To a 9-anthryllithium solution prepared from 5.14 g (0.02 mol) of 9-bromoanthracene and 14 ml of 1.6 *M* *n*-butyllithium (hexane) in 350 ml of diethyl ether freshly distilled from $LiAlH_4$ was added 3.2 g (0.02 mol) of cyclobutyl phenyl ketone. After 1 hr the solution was poured into cold water and extracted with ether, the ether layer was separated and dried and the ether evaporated, and the resulting brown semisolid chromatographed on neutral alumina (1:1 benzene–hexane eluent). The third fraction was carbinol XIV obtained as a yellow oil which crystallized from 1:4 benzene–hexane to give 3 g (45%) of cream-colored crystals: mp 172–173°; ir 3590, 1438, 878, 689 cm^{-1}.

Treatment of the carbinol XIV (2.0 g, 5.9 mol) with 0.1 g (0.39 mmol) of I_2 in 50 ml of benzene under reflux for 16 hr gave, after washing the solution with sodium thiosulfate solution, washing, drying, treatment with decolorizing charcoal, removal of the solvent, and three recrystallizations from 2-propanol–benzene, 1.6 g (85%) of pale yellow needles of the methylenecyclobutane XV: mp 171.5–172.5°; ir 3080, 3055, 3030, 2980, 2955, 2910, 2820, 1650 (w), 1594, 1412 cm^{-1}. The same product was obtained in 71% yield by heating the carbinol XIV for 16 hr in 250 ml of 98% formic acid under reflux. Recrystallization from ethanol gave XV: mp 174–175°; uv max 258 nm (ϵ 220,000), 349 (5350), 367 (10,700); nmr τ 1.75 (s, 0.8), 2.1 (m, 3.9), 2.75 (m, 3.9), 2.91 (s, 5.2), 6.65 (t, 1.9), and 7.82 (m, 4.2).

Anal. Calcd for $C_{25}H_{20}$: C, 93.7; H, 6.3. Found: C, 93.7; H, 6.3.

Treatment of 2.6 g (7.68 mmol) of carbinol XIV with 25 ml of an ice-cold mixture of sulfuric and trifluoroacetic acids (1:1) for 20 min followed by pouring into ice water, extraction with chloroform, drying of the chloroform solution, removal of the solvent, and recrystallization (five times) from absolute ethanol–benzene gave 145 mg (5.9% yield) of hydrocarbon, probably XVII: mp 149–150°; uv (ethanol) max 396 nm (ϵ 8830), 375 (10,200), 356 (6700), 340 (3220), 325 (1430); nmr τ 1.85 (s, 1), 2.00–3.23 (m, 12), 5.01 (s, 1), 7.30–8.33 (m, 6); mass spectrum (rel intensity) *m/e* 320 (56), 292 (100), 291 (50), 215 (73), 28 (>250).

Anal. Calcd for $C_{25}H_{20}$: C, 93.7; H, 6.3. Found: C, 93.6; H, 6.2.

Reduction of the methylenecyclobutane XV (0.16 g, 0.5 mmol) in 80 ml of 1:1 ethanol–ethyl acetate over 0.135 g of 83% PtO_2 with H_2 at 1 atm for 1.5 hr (at which time uptake of H_2 ceased) gave after recrystallization from ethanol 0.11 g (68%) of the reduction product, probably (9,10-dihydro-9-anthryl)phenylmethylcyclobutane, as white crystals: mp 131–132°; uv max 235 nm (ϵ 60,800), 256 (14,700), 293 (6550), 305.

Anal. Calcd for $C_{25}H_{24}$: C, 92.5; H, 7.6. Found: C, 92.7; H, 7.6.

9-Bromo-2,3-dimethylanthracene.—To 6.0 g (0.029 mol) of 2,3-dimethylanthracene[25] in 400 ml of CS_2 cooled in an ice bath was added 3.0 g (0.019 mol) of bromine in 50 ml of CS_2 over a 2.5-hr period. After 1 hr under reflux the solvent was removed to give 7.7 g (93%) of bright yellow crystals of the 9-bromoanthracene: mp 117–118°; nmr τ 1.65 (d, 1), 2.10 (m, 2), 2.35 (m, 1), 2.70 (m, 3), 7.76 (d, 6).

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.4; H, 4.6. Found: C, 67.4; H, 4.6.

(2,3-Dimethyl-9-anthryl)phenylmethylenecyclobutane (XVI).—9-Bromo-2,3-dimethylanthracene (2.73 g, 9.5 mmol) was converted to the carbinol by the same procedure described above for the preparation of the carbinol XIV. The dimethylanthrylcarbinol was not characterized but was heated with 250 ml of 98% formic acid under reflux for 12 hr. Chromatography of the product over neutral alumina (hexane eluent) gave a small amount of dimethylanthracene as the first fraction followed by 1.83 g (55%) of hydrocarbon XVI. Recrystallization from benzene–hexane (1:1) gave XVI as white crystals: mp 214–215°; uv max 253 nm (ϵ 8800), 261 (168,000), 342 (3480), 370 (6960); nmr ($CDCl_3$) τ 1.70 (s, 1), 2.23 (s, 2), 2.65 (m, 3), 2.85 (s, 5), 6.61 (t, 2), 7.58 (d, 6), 7.81 (m, 3).

Anal. Calcd for $C_{27}H_{24}$: C, 93.1; H. 6.9. Found: C, 93.3; H, 7.0.

Registry No.—*cis*-I, 27069-94-9; *trans*-I, 27069-95-0; II, 27067-12-5; III, 27111-60-0; IV, 27067-13-6; V, 27067-14-7; VI, 27067-15-8; *cis*-VII, 27069-96-1; *trans*-VII, 27069-97-2; VIII, 27067-16-9; IX, 27067-17-0; X, 27067-18-1; XI, 27067-19-2; XII, 27067-20-5; XIII, 27111-61-1; XIV, 27069-98-3; XV, 27069-99-4; XVI, 27070-004; XVIIa, 27070-01-5; XVIIb, 27070-12-8; 1-mesityl-1-phenyl-2,2-dimethylethylene, 27070-02-6; (9,10-dihydro-9-anthryl)phenylmethylcyclobutane, 27070-03-7; 9-bromo-2,3-dimethylanthracene, 27111-62-2; mesityldiphenylmethane, 7505-15-9; *meso*-1,2-dimethyl-1,2-bis(2,6-dimethylphenyl)ethane, 25140-35-6; (±)-1,2-dimethyl-1,2-bis(2,6-dimethylphenyl)ethane, 25248-75-3; 9-mesitylfluorene, 18153-40-7; tri(2,6-dimethoxyphenyl)methane, 20460-09-7; 2,6-dichlorobenzal chloride, 81-19-6; 1-(2,4-dimethylphenyl)-5-phenylpentane-1,5-dione, 27070-11-7.

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[25] E. de B. Barnett and F. C. Marrison, *Ber.*, **64**, 535 (1931).