ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of α,β-Epoxy Ketones. II. Migratory Aptitudes[1]

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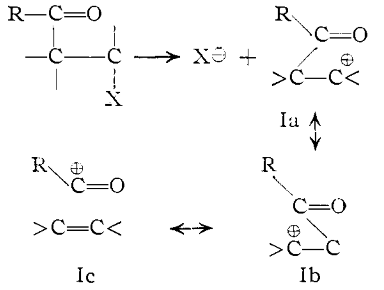
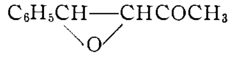
The boron trifluoride-catalyzed isomerizations of three α,β-epoxy ketone systems have been studied. 3,4-Epoxy-4-phenyl-2-butanone yielded 2-phenyl-1,3-butanedione, α-methyl-β-phenylacrylophenone oxide yielded 1,2-diphenyl-1,3-butanedione and α-phenyl-*cis*-benzalacetophenone oxide yielded 1,2,2-triphenyl-1,3-propanedione. Under the same conditions α-phenyl-*trans*-benzalacetophenone oxide was isomerized to benzhydryl phenyl diketone. Possible interpretations of these results are discussed.

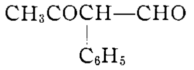
The products obtained from the acid-catalyzed isomerization of several substitued benzalacetophenone oxides were best explained by the assumption that a benzoyl group had migrated in preference to the migration (or elimination) of a hydrogen atom.[2] These results, suggesting the preferential migration of a benzoyl group, are not without precedent. The decarbonylation of diphenyl triketone was found to be explained most readily if the migration of a benzoyl group was assumed.[3] The facile migration of an acyl group to an adjacent electron-deficient center would appear to disagree with a number of studies wherein the migratory tendency of an aryl group has been enhanced by the presence of electron-donating substituents and retarded by the presence of electron withdrawing substituents.[4] However, there is no inherent reason why the migration of an aryl group, a process which probably involves an intermediate phenonium ion,[5] should be comparable with the migration of an alkyl or acyl group. The transition state for the migration of an acyl group could be likened to the formation of a π-complex such as I between an olefin and a Lewis acid. The apparent high order of stability of acyl carbonium ions[6] could be used to justify the importance of contributions from resonance forms such as Ic to transition states of the type I. A similar argument has been used to explain the products obtained from the cleavage of aliphatic ketones with peracids.[7]



Accompanying their discovery that benzalacetophenone oxide could be isomerized to formyldesoxybenzoin in the presence of a sulfuric acid–acetic acid mixture, Weitz and Scheffer described the conversion of benzalacetone oxide (II) to 2-phenyl-1,3-butanedione (III) in the presence of hydrogen chloride.[8] However, Moureu subsequently demonstrated that the product of this reaction was actually 1-phenyl-2,3-butanedione (IV) which was formed *via* the intermediate chlorohydrin V.[9] The same reaction is exemplified by the conversion of benzalacetophenone oxide to benzyl phenyl diketone in the presence of hydrogen chloride.[2,10] Since the isomerization of the epoxy ketone II to the keto aldehyde III would presumably provide an example of the migration of an acetyl group,[11] the rearrangement of the oxide II was reinvestigated. Treatment with an ethereal solution of boron trifluoride converted the epoxy ketone II to the borofluoride complex VI of 2-phenyl-1,3-butanedione. The same product was formed when an authentic sample of the keto aldehyde III was treated with boron trifluoride etherate. Treatment with phenylhydrazine converted the complex VI to 1,4-diphenyl-5-methylpyrazole (VII).



II

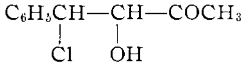


$CH_3COCH(C_6H_5)—CHO$

III

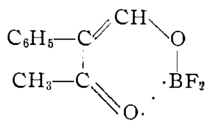
$CH_3COCOCH_2C_6H_5$

IV

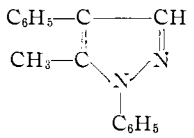


$C_6H_5CH(Cl)—CH(OH)—COCH_3$

V



VI



VII

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 11 to 16, 1955.

[2] H. O. House, THIS JOURNAL, **76**, 1235 (1954).

[3] J. D. Roberts, D. R. Smith and C. C. Lee, *ibid.*, **73**, 618 (1951).

[4] (a) W. E. Bachman and J. W. Ferguson, *ibid.*, **56**, 2081 (1934); (b) J. G. Burr, Jr., and L. S. Ciereszko, *ibid.*, **74**, 5426, 5431 (1952); (c) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952); (d) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (e) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954).

[5] D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949); D. J. Cram and R. Davis, *ibid.*, **71**, 3871 (1949).

[6] (a) R. J. Gillespie, *J. Chem. Soc.*, 2997 (1950); (b) H. Burton and P. F. G. Praill, *ibid.*, 1203, 2034 (1950); *ibid.*, 522, 529, 726 (1951).

[7] W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

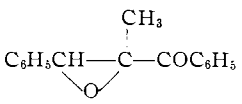
[8] E. Weitz and A. Scheffer, *Ber.*, **54**, 2344 (1921).

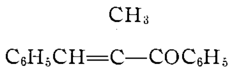
[9] H. Moureu, *Compt. rend.*, **186**, 380, 503 (1928); *Ann. chim. (Paris)*, [10] **14**, 339 (1930).

[10] E. P. Kohler and R. P. Barnes, THIS JOURNAL, **56**, 211 (1934).

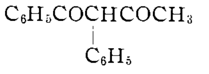
[11] The conversion of the oxides of benzalacetone and benzalacetophenone to the corresponding β-keto aldehydes does not permit one to decide whether the phenyl group or the acyl group has migrated. Although our studies of analogous systems suggest that the acyl group has migrated in each instance, definitive studies employing isotopic labeling techniques have not yet been done.

It was of interest to extend the observation that a benzoyl group would migrate in preference to a hydrogen atom by a comparison of the migratory tendencies of a benzoyl group and an alkyl group. *A priori* the apparent tendency for a hydrogen atom to migrate (or be eliminated) in preference to the migration of an alkyl group[12] would lead to the prediction that a benzoyl group would have a greater tendency to migrate than an alkyl group. A study of the isomerization of α-methyl-β-phenylacrylophenone oxide (VIII) substantiated this prediction.

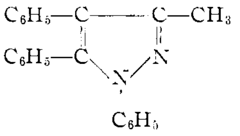

VIII

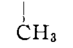

$C_6H_5CH{=}\overset{CH_3}{C}{-}COC_6H_5$

IX

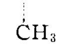

$C_6H_5CO\underset{C_6H_5}{CH}COCH_3$

X


XI


$C_6H_5COCO\underset{CH_3}{CH}C_6H_5$

XII

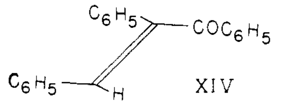

$C_6H_5CH{=}\underset{CH_3}{C}{-}O{-}COC_6H_5$

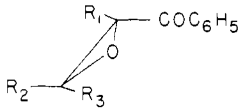
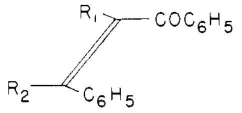
XIII

Only one of the diastereoisomeric forms of the oxide VIII could be isolated from the reaction of the olefin IX with alkaline hydrogen peroxide. When a solution of this epoxy ketone VIII in ether was treated with boron trifluoride as described previously[2] only unchanged starting material could be isolated from the reaction mixture. However, treatment with a cyclohexane solution of boron trifluoride etherate[13] converted the oxide VIII to 1,2-diphenyl-1,3-butanedione (X). The product was converted to 3-methyl-1,4,5-triphenylpyrazole (XI) which was identical with the pyrazole obtained from an authentic sample of the diketone X. Treatment of the crude rearrangement product with *o*-phenylenediamine dihydrochloride failed to yield any of the quinoxaline of 1,3-diphenyl-1,2-butanedione (XII), the product which would have been expected if the methyl group rather than the benzoyl group of the oxide VIII had migrated.

Since 1,2-diphenyl-1,3-butanedione (X), the isomerization product of the above oxide VIII, has also been produced by treatment of the enol benzoate XIII of phenylacetone with gaseous boron trifluoride in an inert solvent,[14] it could be argued that the epoxide isomerizations described are in fact initial isomerizations to enol benzoates such as XIII; the enol esters could then be converted to the 1,3-dicarbonyl compounds[15] which are isolated. Although such a point of view would avoid the direct migration of an acyl group to an electron-deficient center, the involvement of the enol benzoate XIII as an intermediate in the isomerization of the oxirane VIII to the diketone X was found to be untenable. When the enol ester XIII was treated with boron trifluoride etherate in cyclohexane solution, conditions which converted the oxide VIII to the diketone X, the enol benzoate XIII was recovered. In addition no 3-methyl-1,4,5-triphenylpyrazole (XI) could be isolated when the crude, recovered enol ester XIII was treated with phenylhydrazine.

The isomerization products of the *cis*- and *trans*-dypnone oxides and β,β-diphenylacrylophenone oxide indicated that a benzoyl group migrated in preference to a hydrogen atom regardless of the stereochemistry of the starting material.[2] Isomerization of the oxide XV derived from α-phenyl-*trans*-benzalacetophenone (XIV) to benzylhydryl phenyl diketone (XXII) suggested that the phenyl group migrated in preference to the benzoyl group.[2] However, studies which compared the migratory aptitudes of various aryl groups in rearrangements of the pinacol type have revealed that the identity of the migrating group is often determined by the stereochemistry of the starting material.[16] Therefore, a study of the rearrangement of both diastereoisomeric α-phenylbenzalacetophenone oxides (XV and XVI) was of interest. That the oxide derived from α-phenyl-*trans*-benzalacetophenone[17] (XIV) had the *trans* configuration XV was established by the stereospecific synthesis of the *cis* isomer XVI.


XIV



XV, $R_1 = R_2 = C_6H_5$; $R_3 = H$

XVI, $R_1 = R_3 = C_6H_5$; $R_2 = H$

XVIII, $R_1 = H$; $R_2 = R_3 = C_6H_5$

XVIIa, $R_1 = C_6H_5$; $R_2 = H$

b, $R_1 = H$; $R_2 = C_6H_5$

c, $R_1 = R_2 = C_6H_5$

Initial attempts to prepare the *cis*-epoxy ketone XVI involved epoxidation of the corresponding olefin XVIIa with alkaline hydrogen peroxide. Even after extended reaction periods, only the unsaturated ketone XVIIa, accompanied in one instance by benzoic acid, could be isolated from the reaction mixture. Similarly, α,β,β-triphenylacrylo-

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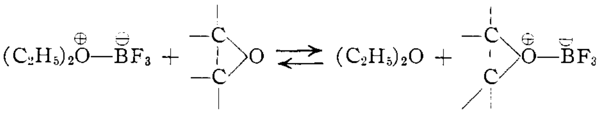
[12] For example see (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 473–523; (b) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 451–534; (c) D. J. Cram, THIS JOURNAL, **74**, 2137 (1952); (d) E. R. Alexander and D. C. Dittmer, *ibid.*, **73**, 1665 (1951); (e) H. O. House, *ibid.*, **77**, 5083 (1955).

[13] Consideration of the equilibrium



will make apparent the possibility that the concentration of the boron trifluoride–oxirane complex may be increased by the use of an inert solvent such as cyclohexane rather than ether. The increased concentration of this complex would justify the increased rate of isomerization observed.

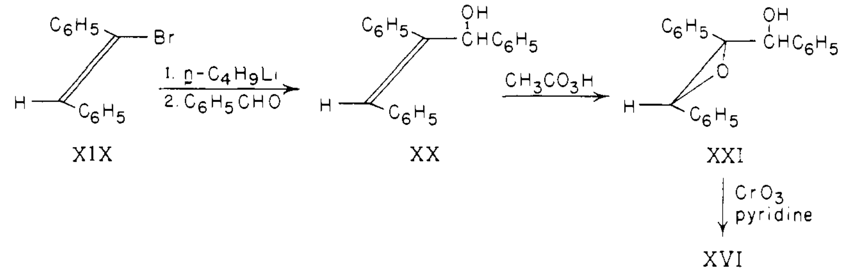
[14] F. G. Young, F. C. Frostick, Jr., J. T. Sanderson and C. R. Hauser, THIS JOURNAL, **72**, 3635 (1950).

[15] C. R. Hauser, F. W. Swamer and J. T. Adams in R. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 59–196.

[16] For a summary of these results see D. Y. Curtin, *Rec. Chem. Prog.*, **15**, 111 (1954).

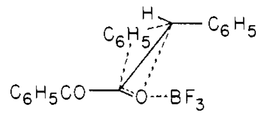
[17] W. B. Block and R. E. Lutz, THIS JOURNAL, **75**, 5990 (1953).

phenone (XVIIc) was recovered unchanged after treatment with alkaline hydrogen peroxide. On the other hand α-phenyl-*trans*-benzalacetophenone (XIV) could be readily converted to the epoxy ketone XV under the same conditions[2] and β,β-diphenylacrylophenone (XVIIb) was converted to the corresponding oxide XVIII in 47% yield by the use of a reaction time of 27 hours. These observations are in agreement with the suggestion[17] that the olefinic double bond in systems of type XVII is attacked very slowly by nucleophilic reagents (in this case the hydroperoxide anion[18]). Moreover, a study of molecular models of the compounds XVIIa and XVIIc where epoxidation was unsuccessful revealed that molecular conformations of these compounds in which the olefinic double bond and the carbonyl group were coplanar were very unfavorable sterically. These coplanar conformations would be required to permit conjugation between the olefinic double bond and the carbonyl group with a consequent ease of nucleophilic attack at the olefinic double bond. Similar coplanar conformations are much more favorable for the unsaturated ketones XIV and XVIIb which can be converted to the corresponding oxides. The ultraviolet spectra of the unsaturated ketones are in accord with these suggestions, the compounds wherein coplanar conformations are more favorable absorbing at appreciably longer wave lengths[17]: XIV, λ_{max} 255 mμ (ϵ_{max} 14,800) and 302 mμ (ϵ_{max} 13,400); XVIIb, λ_{max} 233 mμ (ϵ_{max} 15,100) and 302 mμ (ϵ_{max} 9,500); XVIIa, λ_{max} 260 mμ (ϵ_{max} 24,600) and 281 mμ (ϵ_{max} 23,000); XVIIc, λ_{max} 242 mμ (ϵ_{max} 24,800) with a point of inflection at 280 mμ (ε 12,700).

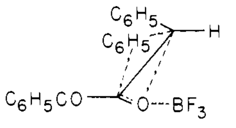


$(C_6H_5)_2CHCOCOC_6H_5$

XXII



XXIII



XXIV

The synthetic procedure employed for the synthesis of the desired *cis*-epoxy ketone XVI was based on α-bromo-*trans*-stilbene (XIX). The lithium compound derived from this bromo olefin has been found upon carbonation to yield α-phenyl-*cis*-cinnamic acid, the bromine atom having been replaced by a carboxyl group without loss of the relative configurations of the groups about the olefinic double bond.[19] Similar results have been obtained with other systems.[20] Our expectation that the alcohol derived from the reaction of benzaldehyde with the lithium salt obtained from the bromo olefin XIX would have the *cis*-configuration XX has recently been confirmed by Lutz and Rinker who prepared the same alcohol by the reduction of the *cis* ketone XVIIa with lithium aluminum hydride.[21] The subsequent epoxidation of the unsaturated alcohol XX to the crystalline *cis*-epoxy alcohol XXI followed by oxidation to the desired ketone XVI is analogous to the reaction sequence recently reported by Wasserman and Aubrey.[22] It is interesting to note that the *trans*-oxide XV, λ_{max} 252.5 mμ (ϵ_{max} 16,400) absorbs ultraviolet light at slightly longer wave lengths and with slightly greater intensity than the *cis*-oxide XVI λ_{max} 252 mμ (ϵ_{max} 15,100) as would be predicted on the basis of similar studies by Cromwell and his co-workers.[23]

The boron trifluoride-catalyzed isomerization of the *trans*-epoxy ketone XV to benzhydryl phenyl diketone (XXII), previously reported[2] in ether solution, has also been effected in cyclohexane solution. A consideration of possible transition states XXIII and XXIV which might be involved in the isomerization of the *trans*(XV)- and *cis*(XVI)-epoxides, respectively, suggested that some benzoyl migration might be observed with the *cis* isomer XVI. In this case the transition state XXIV for phenyl migration requires the energetically undesirable *cis* orientation[16] of the phenyl and benzoyl groups. No such orientation would be required in the corresponding transition state for the migration of a benzoyl group. However, the isomerization of the *cis*-epoxy ketone XVI in the presence of boron trifluoride etherate, either in cyclohexane or ether solution, produced neither of the expected diketones XXII or XXV but rather the keto aldehyde XXVI. The product was shown to be identical with a sample of the keto aldehyde XXVI prepared by the isomerization of β,β-diphenylacrylophenone oxide (XVIII) as described previously.[2] The product readily lost formic acid to yield benzhydryl phenyl ketone (XXVII). The product obtained by the acylation of the sodium enolate of diphenylacetaldehyde with benzoyl chloride has been found not to be the keto aldehyde XXVI as reported,[24] but rather the enol benzoate XXIX of diphenylacetaldehyde.

The enol benzoate XXVIII of desoxybenzoin, the enol benzoate XXIX of diphenylacetaldehyde and

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(18) C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

(19) D. Y. Curtin and E. E. Harris, THIS JOURNAL, **73**, 4519 (1951).

(20) (a) A. S. Dreiding and R. J. Pratt, *ibid.*, **76**, 1902 (1954); (b) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (c) E. A. Braude and C. J. Timmons, *ibid.*, 2000 (1950).

(21) R. E. Lutz and E. H. Rinker, Jr., THIS JOURNAL, **77**, 366 (1955).

(22) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).

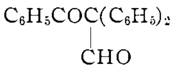
(23) (a) N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952); (b) N. H. Cromwell and co-workers, THIS JOURNAL, **73**, 1044 (1951); (c) N. H. Cromwell and R. A. Setterquist, *ibid.*, **76**, 5752 (1954).

(24) W. Schlenk, H. Hillemann and I. Rodloff, *Ann.*, **287**, 135 (1931).

the diketone XXV have all been excluded as possible intermediates in the rearrangement of either oxide XV or XVI. When the enol ester XXVIII was subjected to the reaction conditions employed for the above isomerizations only the unchanged ester XXVIII and desoxybenzoin could be isolated; similarly, the enol benzoate XXIX was recovered unchanged. When 1,2,3-triphenyl-1,3-propanedione (XXV) was subjected to the same reaction conditions the unchanged diketone XXV was recovered accompanied by a high melting, yellow, fluorescent material whose composition suggested that it has the structure of the borofluoride complex XXX.

$(C_6H_5CO)_2CHC_6H_5$

XXV

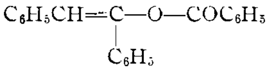


$C_6H_5COC(C_6H_5)_2\text{—}CHO$

XXVI

$C_6H_5COCH(C_6H_5)_2$

XXVII

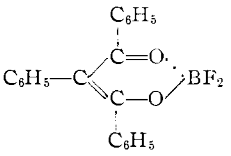


$C_6H_5CH{=}C(C_6H_5)\text{—}O\text{—}COC_6H_5$

XXVIII

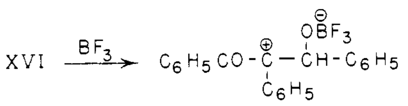
$(C_6H_5)_2C{=}CH\text{—}O\text{—}COC_6H_5$

XXIX

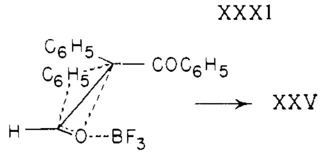


XXX

It would thus appear that the rearrangement of α-phenyl-*cis*-benzalacetophenone oxide (XVI) represents a case wherein the oxirane ring of an α,β-epoxy ketone has been cleaved to produce at least a partial positive charge on the carbon atom alpha to the carbonyl group (*i.e.*, XXXI) in violation of Pauling's adjacent charge rule.[25] It will be noted that a transition state XXXII of the type previously discussed does not require the unfavorable *cis*-orientation of



XXX1



XXXII

bulky groups on adjacent carbon atoms. In addition the positive ion XXXI may be stabilized by resonance with the adjoining phenyl ring.[26]

Experimental[27]

3,4-Epoxy-4-phenyl-2-butanone (II).—The keto oxide, prepared by the epoxidation of *trans*-benzalacetone[28] as described by Weitz and Scheffer,[29] crystallized from a methanol–water mixture as white plates, m.p. 54–55.5° (lit. 52–53°,[9] 54–56°[29]). The infrared spectrum[30] of the oxide exhibits an absorption band at 1710 cm.$^{-1}$ attributable to a carbonyl group. The ultraviolet spectrum has a maximum at 221 mμ (ϵ_{max} 10,200).

Rearrangement of 3,4-Epoxy-4-phenyl-2-butanone.—A solution of 0.50 g. (0.0031 mole) of the keto oxide and 2.0 ml. (0.016 mole) of boron trifluoride etherate in 25 ml. of ether was stirred for 30 minutes and then washed with two portions of water. After the solvent had been removed from the organic layer, the residue was crystallized from petroleum ether (b.p. 90–100°). **The borofluoride complex of 2-phenyl-1,3-butanedione** separated as white needles, m.p. 100–101.5°, yield 0.30 g. (46%). The ultraviolet spectrum of the product exhibits maxima at 227 mμ (ϵ_{max} 8,500), 268 mμ (ϵ_{max} 5,900) and 276 mμ (ϵ_{max} 5,800); the infrared spectrum[30,31] exhibits no band in the 3 μ region attributable to a hydroxyl function. In the 6 μ region a strong band is found at 1625 cm.$^{-1}$ which may be ascribed to a carbon–carbon double bond (or a carbon–oxygen double bond) in a chelate system.[32]

Anal. Calcd. for $C_{10}H_9O_2BF_2$: C, 57.19; H, 4.32; F, 18.10; B, 5.15. Found: C, 57.16; H, 4.21; F, 17.81; B, 5.28.

The same compound, identified by a mixed melting point determination, was formed when an authentic sample[33] of 2-phenyl-1,3-butanedione, m.p. 71–73° (lit. 73–74°,[34] 76°[33]), was treated with boron trifluoride etherate.

In another experiment the crude rearrangement product was treated with a boiling solution of 1.0 ml. of phenylhydrazine and 0.1 g. of sodium acetate in 25 ml. of ethanol. After 20 minutes the boiling solution was diluted with water, decolorized with Norit and cooled. The crude **5-methyl-1,4-diphenylpyrazole** crystallized as light yellow plates, m.p. 157–160°, yield 0.29 g. (40%). Recrystallization afforded the pure pyrazole as white plates melting at 159–160.5°. The ultraviolet spectrum of the pyrazole has a maximum at 253 mμ (ϵ_{max} 18,500).

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.03; H, 6.02; N, 11.96. Found: C, 81.99; H, 6.09; N, 12.08.

An authentic sample of the 2-phenyl-1,3-butanedione was converted to the same pyrazole, the two samples being identified both by a mixed melting point determination and by comparison of their infrared spectra.

α-Methyl-β-phenylacrylophenone Oxide (VIII).—α-Methyl-β-phenylacrylophenone, a light yellow liquid boiling at 154–159° (0.3 mm.), $n^{26}D$ 1.6163, was prepared by the method of Kohler[35] who reported the boiling point to be 190–192° (28 mm.). The ultraviolet spectrum of the unsaturated ketone has maxima at 224 mμ (ϵ_{max} 12,000) and 290 mμ ϵ_{max} 17,800). A solution of 5.00 g. (0.0225 mole) of the unsaturated ketone in 100 ml. of methanol was treated with 10.0 ml. of 30% hydrogen peroxide and 5.0 ml. of 6 *N* aqueous sodium hydroxide. After the mixture had been stirred for 20 hours at room temperature, it was poured into 350 ml. of water and extracted with ether. The ether extract was washed with water, dried over magnesium sulfate and the ether was removed. When a solution of the residue, a viscous oil, in a methanol–water mixture was chilled in Dry Ice, 3.05 g. (57%) of the crude oxide, m.p.

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[25] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 199.

[26] This stabilization would probably also be available to the ion derived from the *trans*-epoxy ketone XV. A study of molecular models suggests that the conformation required for such stabilization (coplanarity of the phenyl ring and the incipient carbonium ion) is slightly less favorable for the *trans*-oxide XV than for the *cis* isomer XVI.

[27] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with a Baird double beam infrared recording spectrophotometer, model B, fitted with a sodium chloride prism. The ultraviolet spectra were determined in 95% ethanol (except where noted) with a Cary recording spectrophotometer, model 11 MS. The microanalyses were performed by Dr. S. M. Nagy and his associates.

[28] G. Gamboni, V. Theus and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

[29] E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

[30] Determined in carbon tetrachloride solution.

[31] Determined as a Nujol mull.

[32] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 126.

[33] M. Roch, *Compt. rend.*, **220**, 322 (1945).

[34] K. von Auwers and H. Lmlewig, *Ann.*, **526**, 130 (1936).

[35] E. P. Kohler, *Am. Chem. J.*, **31**, 642 (1904).

38–50°, separated from the mixture. The pure keto oxide crystallized from hexane solution at Dry Ice temperatures as white prisms, m.p. 53–54°, yield 2.37 g. (44%). The ultraviolet spectrum of the epoxide has a maximum at 247 mμ (ϵ_{max} 13,700); the infrared spectrum[30] has a band at 1685 cm.$^{-1}$ attributable to a conjugated carbonyl group.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.95. Found: C, 80.64; H, 6.00.

Repeated attempts to isolate a second crystalline substance from the mother liquors were unsuccessful. The composition of various fractions of the residual oil (found: C, 82.72, 84.45, 85.31; H, 6.41, 6.40, 6.46) suggested that it was composed predominantly of the unchanged olefin (calcd. for $C_{16}H_{14}O$: C, 86.46; H, 6.35).

Rearrangement of α-Methyl-β-phenylacrylophenone Oxide.—A solution of 0.50 g. (0.0021 mole) of the epoxy ketone and 2.0 ml. (0.016 mole) of boron trifluoride etherate in 25 ml. of ether was boiled under reflux for 30 minutes and then washed with two portions of water. Removal of the solvent from the organic layer left a viscous oil whose infrared spectrum[30] was essentially identical with the spectrum of the starting material. A hexane solution of the crude product, when chilled in Dry Ice, deposited 0.203 g. (41% recovery) of the epoxy ketone, m.p. 49–52°. Recrystallization afforded the pure oxide, m.p. 53–54°, whose identity was confirmed by a mixed melting point determination with an authentic sample.

A mixture of 0.50 g. (0.0021 mole) of the oxide, 2.0 ml. (0.016 mole) of boron trifluoride etherate and 25 ml. of cyclohexane was stirred for 10 minutes, diluted with ether and washed with two portions of water. After the solvents had been removed the crude product was sublimed *in vacuo* (100° at 0.1 mm.). The sublimate, a light yellow crystalline solid melting at 58–77°, amounted to 0.41 g. The product separated from hexane solution as white needles, m.p. 82–85°, yield 0.33 g. (66%). A subsequent crystallization from hexane gave the pure enol form of **1,2-diphenyl-1,3-butanedione**, m.p. 88–89°. The compound gives an immediate red-violet color with ferric chloride. The ultraviolet spectrum of the product exhibits maxima at 234 mμ (ϵ_{max} 9,400) and 312 mμ (ϵ_{max} 12,100). In the 3 μ region of the infrared spectrum[30] no distinct band attributable to a hydrogen–oxygen stretching vibration can be selected. In the 6 μ region one especially broad band with its maximum absorption at 1610 cm.$^{-1}$ is found.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.50; H, 5.76.

When a hexane solution of the pure enol form was allowed to evaporate slowly a mixture of crystalline forms, m.p. 67–76°, was obtained. The infrared spectrum[31] of this mixture exhibits two additional bands at 1690 and 1715 cm.$^{-1}$ attributable to a conjugated and an unconjugated carbonyl group, respectively.

An almost identical spectrum[30] was obtained from the crude rearrangement product (before sublimation). No quinoxaline derivative could be isolated when a sample of the same crude reaction product was treated with *o*-phenylenediamine dihydrochloride in the manner described below. However, when the crude product was treated with phenylhydrazine as described previously 0.39 g. (60%) of **3-methyl-1,4,5-triphenylpyrazole** was obtained as white needles, m.p. 184.5–186°. Recrystallization from hexane raised the melting point to 185.5–186.5°. The ultraviolet spectrum of the product, which exhibits a maximum at 264 mμ (ϵ_{max} 17,100) with a point of inflection at 233 mμ (ϵ 21,200), is almost identical with the spectrum of the known 1,4,5-triphenylpyrazole[2] wherein the maximum and the point of inflection are found at 265 mμ (ϵ_{max} 15,700) and 233 mμ (ϵ 21,200), respectively.

Anal. Calcd. for $C_{22}H_{18}N_2$: C, 85.12; H, 5.84; N, 9.03. Found: C, 85.38; H, 5.68; N, 8.82.

An authentic sample of 1,2-diphenyl-1,3-butanedione was prepared according to the method of Young, Frostick, Sanderson and Hauser[14] who reported the compound to melt at 76–77°. Our preparation crystallized from methanol-water as a mixture of crystalline forms, m.p. 75–88°. The product was therefore converted to 3-methyl-1,4,5-triphenylpyrazole which was shown to be identical with the previous pyrazole sample both by a mixed melting point determination and a comparison of the infrared spectra of the two samples. It seems probable that the crystalline form melting at 76–77° is the diketo modification of 1,2-diphenyl-1,3-butanedione whereas the form melting at 88–89° is one of the enol forms. The acylation of the sodium salt of desoxybenzoin with acetyl chloride has been reported[36] to yield 1,2-diphenyl-1,3-butanedione as needles melting at 99–99.5°. However, the fact that their product yielded the oxime of desoxybenzoin rather than an isoxazole with hydroxylamine suggests that their compound was actually the enol acetate of desoxybenzoin which has been reported[37] to melt at 101°. The formation of such enol esters during the attempted acylation of ketones has been observed[15] in other instances (see the acylation of diphenylacetaldehyde described below).

Treatment of the Enol Benzoate XIII of Phenylacetone with Boron Trifluoride Etherate.—A solution of 0.50 g. (0.0021 mole) of the enol benzoate, b.p. 193–196° (11 mm.), n^{25}D 1.5871 [lit.[14] b.p. 185–189° (10 mm.), n^{25}D 1.5872], in cyclohexane was treated with 2.0 ml. (0.016 mole) of boron trifluoride etherate and then worked up in the manner described previously. The infrared spectrum[30] of the residual oil is essentially identical with the spectrum of the initial enol benzoate and differs markedly from the spectrum of 1,2-diphenyl-1,3-butanedione. No 3-methyl-1,4,5-triphenylpyrazole could be isolated when a portion of the crude recovered enol ester was treated with phenylhydrazine as described previously.

2-Phenyl-3-(1-phenylethyl)-quinoxaline.—A solution of 1.00 g. (0.0042 mole) of *trans*-dypnone oxide[38] (m.p. 91.5–93°) in 35 ml. of boiling ethanol was treated with 5.0 ml. of 6 *N* aqueous sodium hydroxide. The mixture was boiled for 1 minute and then poured into a mixture of ice and sulfuric acid. The resulting mixture was extracted with ether, the extract dried over magnesium sulfate and the solvent removed. A mixture of the residual yellow oil[39] with 1.0 g. of *o*-phenylenediamine dihydrochloride and 50 ml. of ethanol was boiled for 30 minutes, diluted with water and decolorized with Norit. The quinoxaline separated from the cold solution as white needles, m.p. 117–118°, yield 0.52 g. (40%). An additional crystallization raised the melting point to 117.5–118.5°. The ultraviolet spectrum of the compound exhibits maxima at 239 mμ (ϵ_{max} 35,400) and 323 mμ (ϵ_{max} 10,300).

Anal. Calcd. for $C_{22}H_{18}N_2$: C, 85.12; H, 5.84; N, 9.03. Found: C, 85.01; H, 5.72; N, 9.17.

Epoxidation Studies.—To determine the stability of methanolic solutions of sodium hydroperoxide an equimolar mixture of 6 *N* aqueous sodium hydroxide and 30% hydrogen peroxide in methanol was prepared. The initial peroxide content of the mixture was 0.0055 mmole/ml. After an aliquot of the solution had been allowed to stand at 40° for 3.5 hours the peroxide content was 0.00089 mmole/ml. (12% of the initial concentration). Another aliquot was allowed to stand at room temperature (*ca.* 27°); after 3.5 hours the peroxide content was 0.0029 mmole/ml. (53% of the initial value) and after 13 hours 0.0011 mmole/ml. (20% of the initial value).

A mixture of 1.00 g. (0.0035 mole) of β,β-diphenylacrylophenone, m.p. 86–87.5° (lit.[40] 86–87°), λ_{max} 233 mμ (ϵ_{max} 15,100) and 302 mμ (ϵ_{max} 9,500), 4.0 ml. of 30% hydrogen peroxide, 2.0 ml. of 6 *N* aqueous sodium hydroxide and 60 ml. of methanol was stirred for 27 hours at room temperature. Additional 3-ml. portions of hydrogen peroxide were added after 6, 10 and 22 hours. After the reaction mixture had been poured into water, the precipitated solid was recrystallized from an acetone–water mixture. The crude β,β-diphenylacrylophenone oxide separated as white prisms, m.p. 121.5–124°, yield 492 mg. (46.6%). Recrystallization raised the melting point to 123.5–124.5° (lit.[41] 124–125°). The melting point of a mixture of the product with an authentic sample[41] was not depressed. When a reaction

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[36] G. Wittig, F. Bangert and H. Kleiner, *Ber.*, **61**, 1140 (1928).

[37] R. P. Barnes, S. R. Cooper, V. J. Tulane and H. Delaney, *J. Org. Chem.*, **8**, 153 (1943).

[38] H. H. Wasserman, N. E. Aubrey and H. E. Zimmerman, THIS JOURNAL, **75**, 96 (1953).

[39] The preparation of crude 1,3-diphenyl-1,2-butanedione has been reported by Kohler and Barnes (ref. 10).

[40] P. L. Southwick, L. A. Pursglove and P. Numerof, THIS JOURNAL, **72**, 1600 (1950).

[41] E. P. Kohler, N. K. Richtmyer and W. F. Hester, *ibid.*, **53**, 205 (1931).

time of 1 hour was employed for the expoxidation only the starting material could be isolated.

In a similar manner 2.00 g. (0.0056 mole) of α,β,β-triphenylacrylophenone,[42] m.p. 150–151.5° (lit.[40] 148°), λ_{max} 242 mμ (ϵ_{max} 24,800) and a point of inflection at 280 mμ (ϵ 12,700), was treated with a methanolic solution of hydrogen peroxide and sodium hydroxide, the total reaction time being 1 week. Only the starting ketone, 1.97 g. (99% recovery), m.p. 149.5–151.5°, could be isolated from the reaction mixture.

In the same way samples of α-phenyl-*cis*-benzalacetophenone, m.p. 87.5–88.5° (lit.[40] 88–89°), λ_{max} 260 mμ (ϵ_{max} 24,600) and 281 mμ (ϵ_{max} 23,000), were treated with methanolic solutions of sodium hydroxide and hydrogen peroxide at room temperature for 24, 96 and 367 hours, the starting material being recovered to the extent of 81, 64 and 60%, respectively. In the case of the 367-hour run where an 0.70-g. (0.0026 mole) sample of the unsaturated ketone was employed 0.10 g. of benzoic acid was also isolated. In a subsequent run at 40° after 13 hours 88% of the starting ketone was recovered.

Rearrangement of α-Phenyl-*trans*-benzalacetophenone Oxide (XV) in Cyclohexane Solution.—A suspension of 1.00 g. (0.0033 mole) of the oxide,[2] m.p. 82.5–83.5°, λ_{max} 252.5 mμ (ϵ_{max} 16,400) and 4.0 ml. (0.032 mole) of boron trifluoride etherate in 25 ml. of cyclohexane was stirred for 5 minutes, diluted with ether and washed with two portions of water. After the solvent had been removed from the organic layer, the residual oil was treated with 1.2 g. of *o*-phenylenediamine dihydrochloride as described earlier. The **2-phenyl-3-benzhydrylquinoxaline** separated as pink crystals, m.p. 197–199.5°, yield 1.00 g. (80.7%). Recrystallization gave 957 mg. (77.2%) of the pure quinoxaline, m.p. 198–199.5°, whose identity was established by a mixed melting point determination with an authentic sample.[2] When reaction times of 10 and 2 minutes were employed the quinoxaline was isolated in 69 and 66% yield, respectively. A solution of the crude rearrangement product, a yellow oil, in a mixture of petroleum ether (b.p. 30–60°) and ether when chilled in Dry Ice, deposited **benzhydryl phenyl diketone** as yellow crystals, m.p. 47.5–48.5° (lit.[43] 49–50°). The infrared spectrum[44] of the product exhibits bands at 1710 and 1665 (1655)[45] cm.$^{-1}$ attributable to a non-conjugated and a conjugated carbonyl group, respectively. The ultraviolet spectrum has a maximum at 261 mμ (ϵ_{max} 10,900).

1,2,3-Triphenylallyl Alcohol (XX).—To a cold (−35°) solution of 6.0 g. (0.023 mole) of α-bromo-*trans*-stilbene, m.p. 31–32° (lit.[46] 31°), in a 2:3 (by volume) benzene–ether mixture was added dropwise and with stirring, a solution of 0.027 mole of butyllithium[47] in 30 ml. of ether. The temperature of the solution was not allowed to rise above −20°. After the addition was complete, the solution was stirred for 5 minutes and then treated, dropwise and with stirring, with a solution of 2.4 g. (0.022 mole) of benzaldehyde in 10 ml. of ether. The resulting mixture was stirred for 2 hours at −35°, allowed to warm to 0° and then poured into an ice-cold, saturated solution of ammonium chloride in water. The organic layer was separated, dried over magnesium sulfate and the solvents were removed under reduced pressure. The residual 1,2,3-triphenylallyl alcohol crystallized from petroleum ether (b.p. 30–60°) as white plates, m.p. 98.2–99.2° (lit.[21] 101°), yield 5.4 g. (82%). The ultraviolet spectrum of the product has a maximum at 261 mμ (ϵ_{max} 16,300) (lit.[21] 262 mμ (ϵ_{max} 16,000)); the infrared spectrum[45] has a strong band at 3200 cm.$^{-1}$ attributable to an associated hydroxy group.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.32; H, 6.40.

2,3-Epoxy-1,2,3-triphenyl-1-propanol (XXI).—To a mixture of 4.0 g. (0.014 mole) of 1,2,3-triphenylallyl alcohol, 2.5 g. of sodium acetate trihydrate and 75 ml. of chloroform, cooled to 2°, was added dropwise and with stirring, a 40% solution of peracetic acid (3.6 g., 0.048 mole) in acetic acid. The mixture was stirred for 5 hours at 2° and for an additional 60 hours at room temperature. The resulting mixture was washed with water, a saturated aqueous sodium bicarbonate solution and again with water. After the organic phase had been dried over magnesium sulfate, the solvent was removed under reduced pressure. The residual 2,3-epoxy-1,2,3-triphenyl-1-propanol crystallized from an ether–petroleum ether (b.p. 30–60°) mixture as white plates, m.p. 127.6–128.4°, yield 3.32 g. (76%). The ultraviolet spectrum has a maximum at 258 mμ (ϵ_{max} 625); the infrared spectrum[45] has a band at 3450 cm.$^{-1}$ attributable to a hydroxyl group.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.43; H, 6.00. Found: C, 83.17; H, 6.03.

α-Phenyl-*cis*-benzalacetophenone Oxide (XVI).—A solution of 2.9 g. (0.0096 mole) of 2,3-epoxy-1,2,3-triphenyl-1-propanol in 30 ml. of pyridine was added in four portions to a fivefold excess of the chromium trioxide–pyridine complex[48] prepared from 100 ml. of pyridine and 10 g. (0.10 mole) of chromium trioxide, the temperature of the mixture being kept below 15°. After the mixture had been swirled at frequent intervals for 30 minutes, the reaction flask was stoppered and allowed to stand for 16 hours. The resulting mixture was poured into ice-water and extracted with four 40-ml. portions of chloroform. The combined extracts were washed first with dilute hydrochloric acid and then with an aqueous sodium bicarbonate solution and finally dried over magnesium sulfate. After the chloroform had been removed under reduced pressure, the residue was recrystallized from hexane. The α-phenyl-*cis*-benzalacetophenone oxide crystallized as white needles melting at 115.6–116.2°, yield 2.2 g. (76%). The infrared spectrum[44] of the oxide exhibits a band at 1680 cm.$^{-1}$ (conjugated carbonyl group) and has no band in 3 μ region attributable to a hydroxyl group. The ultraviolet spectrum has maxima at 227 mμ (ϵ_{max} 21,350) and 252 mμ (ϵ_{max} 15,100).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.99; H, 5.37. Found: C, 84.18; H, 5.44.

1,2,2-Triphenyl-1,3-propanedione (XXVI).—An ether solution of β,β-diphenylacrylophenone was isomerized in the presence of boron trifluoride etherate as previously described.[2] The crude keto aldehyde crystallized from hexane as white needles, m.p. 103–106°. Recrystallization sharpened the melting point to 105–106°. The infrared spectrum[44] of the product exhibits bands at 1660 cm.$^{-1}$ (conjugated carbonyl group), 1715 cm.$^{-1}$ (unconjugated carbonyl group) and 2800 cm.$^{-1}$ (carbon–hydrogen stretching vibration of an aldehyde). The ultraviolet spectrum has a maximum at 253 mμ (ϵ_{max} 11,600).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.99; H, 5.37. Found: C, 83.78; H, 5.46.

A solution of 30 mg. (0.1 mmole) of the keto aldehyde and 30 mg. of anhydrous sodium acetate in 15 ml. of ethanol was boiled under reflux for 2 hours. The resulting solution was diluted with water. **Phenyl benzhydryl ketone** crystallized from the cold solution as white needles, m.p. 134.5–136°, yield 24 mg. (89%). The melting point of a mixture of the product with the sample previously reported[2] was not depressed.

A solution of 88 mg. (0.29 mmole) of the keto aldehyde, 88 mg. (0.45 mmole) of 2,4-dinitrophenylhydrazine and 0.5 ml. of concentrated hydrochloric acid in ethanol was boiled for 5 minutes and allowed to cool. The crude product, separated by filtration, was recrystallized from an ethanol–chloroform mixture. The **mono-2,4-dinitrophenylhydrazone of 1,2,2-triphenyl-1,3-propanedione** separated as yellow needles, m.p. 225.6–226.5°, yield 126 mg. (90%). The infrared spectrum[44] of the 2,4-dinitrophenylhydrazone exhibits a band at 1665 cm.$^{-1}$ attributable to a conjugated carbonyl group as well as a band at 3100 cm.$^{-1}$ attributable to an associated nitrogen–hydrogen single bond. However, the band found at 1715 cm.$^{-1}$ in the keto aldehyde spectrum is no longer present.

Anal. Calcd. for $C_{27}H_{20}O_5N_4$: C, 67.49; H, 4.20; N, 11.66. Found: C, 67.21; H, 4.34; N, 11.66.

Rearrangement of α-Phenyl-*cis*-benzalacetophenone Oxide (XVI). A. Rearrangement in Ether Solution.—A solution of 0.50 g. (0.0017 mole) of the oxide and 2.0 ml. (0.016

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(42) E. P. Kohler and E. M. Nygaard, THIS JOURNAL, **52**, 4128 (1930).

(43) E. P. Kohler and N. Weiner, *ibid.*, **56**, 434 (1934).

(44) Determined in chloroform solution.

(45) Determined as a suspension in a potassium bromide pellet.

(46) E. Bergmann, *J. Chem. Soc.*, 402 (1936).

(47) H. Gilman and co-workers, THIS JOURNAL, **71**, 1499 (1949).

(48) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *ibid.*, **75**, 422 (1953).

mole) of boron trifluoride etherate in 15 ml. of ether was boiled under reflux for 30 minutes and then diluted with ether. After the resulting solution had been washed with a saturated, aqueous sodium bicarbonate solution and then with water, the organic phase was dried over magnesium sulfate and the solvent was removed. The residual oil crystallized from hexane as white needles melting at 105.2–106.2°, yield 230 mg. (46%). The product was shown to be **1,2,2-triphenyl-1,3-propanedione** both by a mixed melting point determination and by comparison of the infrared spectra of the two samples. The mother liquors from the above recrystallization were treated with a boiling ethanolic solution of sodium acetate as described earlier. Benzhydryl phenyl ketone, identified by a mixed melting point with an authentic sample, crystallized from the cold solution, m.p. 133–135°, yield 0.10 g. (23%). Thus the total yield of the rearrangement product amounted to 79%.

In another experiment the reaction mixture obtained from the isomerization of 60 mg. (0.20 mmole) of the oxide was treated directly with 80 mg. (0.41 mmole) of 2,4-dinitrophenylhydrazine in the manner previously described. The mono-2,4-dinitrophenylhydrazone of 1,2,2-triphenyl-1,3-propanedione, identified by a mixed melting point determination with an authentic sample, was isolated as yellow needles, m.p. 225.6–226.2°, yield 77 mg. (75%).

B. **Rearrangement in Cyclohexane Solution.**—A mixture of 0.50 g. (0.0017 mole) of the oxide and 2.0 ml. (0.016 mole) of boron trifluoride etherate in 15 ml. of cyclohexane was stirred for 5 minutes at room temperature, diluted with ether and the reaction mixture worked up as described earlier. The products, identified by mixed melting point determinations with authentic samples, were **1,2,2-triphenyl-1,3-propanedione**, m.p. 104.8–105.8°, yield 0.19 g. (34%), and **benzhydryl phenyl ketone**, m.p. 132.6–135.6°, yield 40 mg. (9%); the over-all yield was 43% of the theoretical amount.

When the reaction mixture obtained from the isomerization of 60 mg. (0.20 mmole) was treated with 2,4-dinitrophenylhydrazine in the usual manner, the mono-2,4-dinitrophenylhydrazone of 1,2,2-triphenyl-1,3-propanedione was isolated, m.p. 225–226°, yield 44 mg. (46%).

1,2,3-Triphenyl-1,3-propanedione (XXV).—This diketone, prepared by the procedure of Bartlett and Cohen,[49] crystallized from ethanol as white needles, m.p. 151.6–152.6° (lit. 144.5–145.6°,[49] 149°[50,51] 148–151°[52]). Although the melting point of our product corresponds to the melting point (152°) reported[52] for the chemically similar triketone, tribenzoylphenylmethane, the composition of our sample indicates that it is the diketone rather than the triketone.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.99; H, 5.37. Found: C, 83.93; H, 5.48.

The ultraviolet spectrum of the diketone has a maximum at 249 mμ ($\epsilon_{\max}$ 26,400); the infrared spectrum[44] has two absorption bands of approximately equal intensity in the carbonyl region at 1660 and 1685 cm.$^{-1}$. No band attributable to a hydroxyl group is present in the 3 μ region of the spectrum.

A 1.0-g. (0.0033 mole) sample of the diketone was treated with 4.0 ml. (0.032 mole) of boron trifluoride etherate in cyclohexane as described earlier. The insoluble **borofluoride complex of 1,2,3-triphenyl-1,3-propanedione** was separated from the crude reaction product. The complex crystallized from chloroform as yellow, fluorescent needles, m.p. 311–314°, yield 0.61 g. (54%); recrystallization from chloroform raised the melting point of the complex to 313–315°. The ultraviolet spectrum of the product has a maximum (determined in ethanol solution) at 248 mμ ($\epsilon_{\max}$ 23,700) as well as maximum (determined in chloroform solution) at 315 mμ ($\epsilon_{\max}$ 10,600) and 381 mμ ($\epsilon_{\max}$ 24,900). The infrared spectrum[31,45] of the product has no band in the 3 μ region attributable to a hydroxyl function. In the 6 μ region the band of shortest wave length is found at 1600 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{15}O_2BF_2$: C, 72.43; H, 4.34; B, 3.12; F, 10.91. Found: C, 72.25; H, 4.36; B, 2.86; F, 10.95.

From the mother liquors of the above separation was recovered 0.43 g. (43%) of the unchanged diketone, m.p. 152.3–153.3°, identified by a mixed melting point determination.

Similarly, the treatment of 0.25 g. (0.83 mmole) of the diketone with 2.0 ml. (0.016 mole) of boron trifluoride etherate in ether solution yielded 10 mg. (3.4%) of the borofluoride complex, m.p. 311–314°, accompanied by 0.24 g. (96%) of the unchanged diketone, m.p. 149–150°.

1,2-Diphenylvinyl Benzoate (XXVIII).—A mixture of 5.0 g. (0.026 mole) of desoxybenzoin and 3.6 g. (0.026 mole) of benzoyl chloride was heated to 190° for 3 hours, cooled and poured into water. The resulting mixture was extracted with ether and the ether extract was washed with saturated, aqueous sodium bicarbonate solution and then with water. After the organic layer had been dried over magnesium sulfate, the ether was removed and the residual oil crystallized from hexane. The 1,2-diphenylvinyl benzoate separated as white needles, m.p. 120.6–121.6°, yield 1.5 g. (19.5%). The infrared spectrum[44] of the product has bands at 1720 cm.$^{-1}$ (carbonyl group of a conjugated ester), 1635 cm.$^{-1}$ (carbon–carbon double bond) and 1240 cm.$^{-1}$ (carbon–oxygen–carbon grouping of an ester). There are no bands in the 3 μ region of the spectrum which can be attributed to a hydroxyl function. The ultraviolet spectrum has maxima at 227 mμ ($\epsilon_{\max}$ 24,100) and 287 mμ ($\epsilon_{\max}$ 26,500).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.99; H, 5.37. Found: C, 83.88; H, 5.35.

When an 0.25-g. (0.83 mmole) sample of the enol benzoate was treated with 1.0 ml. (0.008 mole) of boron trifluoride etherate in ether solution, the unchanged enol benzoate, 72 mg. (35%), m.p. 120–121°, was recovered accompanied by 40 mg. (23%) of desoxybenzoin, m.p. 58–59°. When the mother liquors were treated with 2,4-dinitrophenylhydrazine, an additional 72 mg. (23%) of **desoxybenzoin 2,4-dinitrophenylhydrazone**, m.p. 202–203°, was isolated. Each of the compounds obtained from the reaction mixture was identified by a mixed melting point determination with an authentic sample.

A similar result was obtained when the enol ester was treated with boron trifluoride in cyclohexane solution, the unchanged enol benzoate, 172 mg. (69%), m.p. 120–121°, and desoxybenzoin 2,4-dinitrophenylhydrazone, 36 mg. (11.5%), m.p. 202–203°, being isolated.

2,2-Diphenylvinyl Benzoate (XXIX).—To a solution of 2.0 g. (0.010 mole) of diphenylacetaldehyde, b.p. 110° (4 mm.), $n^{25}\text{D}$ 1.5882, prepared by the isomerization of *trans*-stilbene oxide in the presence of boron trifluoride etherate,[53] in 30 ml. of ether was added 0.24 g. (0.010 mole) of sodium hydride. After the mixture had been allowed to stand at room temperature with frequent shaking for 12 hours, 2.4 g. (0.017 mole) of benzoyl chloride was added and the mixture was stirred for 10 minutes. After the mixture had been treated with isopropyl alcohol to destroy the unchanged sodium hydride, the mixture was diluted with water. The organic layer was washed with water, a saturated, aqueous sodium bicarbonate solution and, again, with water. The ether solution was dried over magnesium sulfate and then the ether was removed to leave a viscous residue which was taken up in boiling methanol. The 2,2-diphenylvinyl benzoate crystallized as white needles melting at 98.6–99.2°, yield 1.3 g. (39%). The compound previously prepared by the reaction of the sodium enolate (formed by the use of triphenylmethylsodium) of diphenylacetaldehyde with benzoyl chloride was reported to melt at 98–99°.[24] The infrared spectrum[44] of our product has bands at 1710 cm.$^{-1}$ (carbonyl group of a conjugated ester), 1630 cm.$^{-1}$ (carbon–carbon double bond) and 1255 cm.$^{-1}$ (carbon–oxygen–carbon grouping of an ester). There are no bands in the 3 μ region of the spectrum which can be attributed either to a hydroxyl group or to the carbon–hydrogen stretching vibration of an aldehyde. The ultraviolet spectrum of the compound has maxima at 231 mμ ($\epsilon_{\max}$ 25,000), and 279 mμ ($\epsilon_{\max}$ 14,100).

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 83.99; H, 5.37. Found: C, 84.21; H, 5.47.

Samples (0.25 g., 0.83 mmole) of the enol benzoate were treated with 1.0-ml. (0.008 mole) portions of boron trifluoride etherate in the manner outlined above. When cyclohexane was employed as the solvent 221 mg. (89%) of

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[49] P. D. Bartlett and S. G. Cohen, *J. Org. Chem.*, **4**, 88 (1939).

[50] J. Marshall, *J. Chem. Soc.*, **107**, 509 (1915).

[51] S. Goldschmidt and F. Nagel, *Ber.*, **63**, 1212 (1930).

[52] J. Meisenheimer and K. Weibezahn, *ibid.*, **54**, 3195 (1921).

[53] H. O. House, THIS JOURNAL, **77**, 3070 (1955).

the unchanged enol ester, m.p. 98.6–99.6°, was recovered; the recovery amounted to 225 mg. (90%) of the unaltered enol benzoate, m.p. 98.6–99.4°, when ether was the solvent used. Both samples were identified by mixing melting point determinations with the authentic enol benzoate.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Unsaturated Sulfonic Acids. V.[1] Addition of Diazomethane and Phenyl Azide to Derivatives of Ethylenesulfonic Acid and its Homologs[2]

BY CHRISTIAN S. RONDESTVEDT, JR., AND PAULINE K. CHANG

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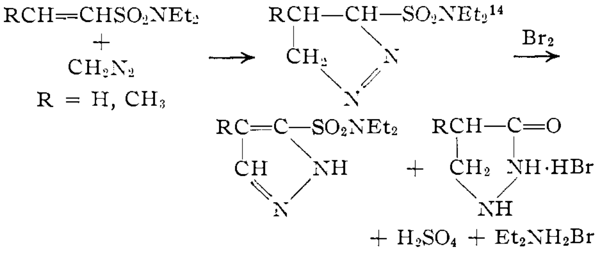
Diazomethane adds to derivatives and homologs of ethylenesulfonic acid to form pyrazoline-3-sulfonic acid derivatives. Pyrazoline-3-diethylsulfonamide on bromination gives pyrazole-3-diethylsulfonamide and 3-pyrazolidone in 2:1 ratio. *n*-Butyl pyrazoline-3-sulfonates on bromination give pyrazole-3-sulfonic acids and butyl bromide. Pyrazoline-3-sulfonyl chloride is unstable and appears to lose sulfur dioxide, forming 3-chloropyrazoline which undergoes conjugate addition to a second mole of ethylenesulfonyl chloride. Phenyl azide adds to N,N-diethylethylenesulfonamide normally to form 1-phenyl-1,2,3-triazoline 4-diethylsulfonamide. Phenyl azide reacts with *two* moles of ethylenesulfonyl chloride or propene-2-sulfonyl chloride, even in the presence of excess phenyl azide, to form 2-(1-phenyl-1-prototriazol-3-yl)-ethanesulfonate (VIa) or its 4,α-dimethyl homolog VIb. VIa was also formed quantitatively by addition of 1-phenyltriazole to ethylenesulfonyl chloride. These reactions are interpreted as a novel form of conjugate addition of a dipolar form of the triazoline or triazole. α-Bromoethylenesulfonyl chloride adds phenyl azide to form the unstable 1-phenyl-4-bromotriazoline-4-sulfonyl chloride which aromatizes promptly by loss of sulfur dioxide and hydrogen chloride to 1-phenyl-4-bromotriazole.

α,β-Unsaturated sulfonic acid derivatives add many nucleophilic reagents readily.[3–5] Diazomethane behaves as a nucleophilic reagent when adding to unsaturated systems,[6,7] and azides appear to react in a similar manner.[7–9] It was therefore of interest to explore the addition of diazomethane and phenyl azide to unsaturated sulfonic acid derivatives. These additions would afford convenient syntheses of derivatives of the unfamiliar pyrazoline-3-sulfonic acids and 1-phenyl-1,2,3-triazoline-4-sulfonic acids. A similar reaction, addition of diazomethane to vinyl *p*-tolyl sulfone, furnished 3-*p*-toluenesulfonylpyrazoline.[10]

Reactions of Diazomethane.—Ethylenesulfonic acid derivatives and homologs were selected for study, since preliminary experiments[11] had shown that derivatives of β-phenylethylenesulfonic acid added diazomethane at an inconveniently slow rate. Derivatives of ethylenesulfonic acid have been described previously[1,12] and the corresponding derivatives of propene-1-sulfonic acid were prepared similarly. It was more convenient to prepare propene-2-sulfonyl chloride by low-temperature dehydrochlorination[1] of 1-chloropropane-2-sulfonyl chloride than by the previously published method.[13]

Addition to Sulfonamides.—N,N-Diethylethylenesulfonamide and N,N-diethylpropene-1-sulfonamide absorbed a molar equivalent of diazomethane slowly (1–4 days) at room temperature. The crude pyrazolines were formed in quantitative yields but, since they could not be purified by distillation or crystallization, they were characterized by aromatization to the corresponding pyrazoles. Jacobs[6] noted that the most satisfactory method for converting pyrazolines to pyrazoles was bromination.

The action of bromine upon crude pyrazoline-3-diethylsulfonamide produced pyrazole-3-diethylsulfonamide in 57% yield, together with 3-pyrazolidone hydrobromide in 30% yield and comparable amounts of sulfuric acid and diethylamine hydrobromide, plus about 4% of hydrazine sulfate. Similarly, 4-methylpyrazoline-3-diethylsulfonamide yielded 4-methylpyrazole-3-diethylsulfonamide in 57% yield, together with diethylamine hydrobromide and sulfuric acid in 18% yield, and 4% of hydrazine sulfate. Only a trace of 4-methylpyrazolidone hydrobromide was isolated, probably because its physical properties render it more difficult to separate from other products of the reaction. The pyrazolidone salts were identified by comparison with authentic samples.



Addition to Sulfonate Esters.—*n*-Butyl ethylenesulfonate and *n*-butyl propene-1-sulfonate absorbed a molar equivalent of diazomethane in 3–5 hr. at room temperature. The pyrazolines were formed in quantitative yield, but they could not be purified

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[6] T. L. Jacobs, chapter on Pyrazoles in R. C. Elderfield, Editor, "Heterocyclic Compounds," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1956. We are indebted to Prof. Elderfield for making the manuscript of this chapter available prior to publication.

[7] L. I. Smith, *Chem. Revs.*, **23**, 193 (1938).

[8] J. H. Boyer and F. C. Canter, *ibid.*, **54**, 41 (1954).

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[11] Unpublished experiments with T. Y. Yu in this Laboratory.

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[13] J. M. Stewart and H. P. Cordts, *ibid.*, **74**, 5880 (1952).

[14] No attempt is made to assign the Δ^1- or Δ^2-structure to the pyrazolines. A discussion of isomerism in pyrazolines is given by Jacobs.[6] See also reference 10.