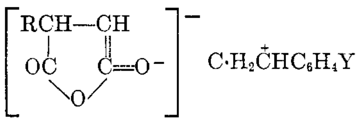
fore, of interest to compare the effect of four more substituents, whose σ- and σ^+-constants are not equivalent, with (2). Fig. 3 gives the experimental points for *p*-chloro, *p*-*t*-butyl, *p*-phenyl and *p*-methyl substituents on the basis of both σ- and σ^+-constants. On the basis of σ-constants, the total deviation for the four points is 0.40 log unit. On the basis of σ^+-constants, the deviation is 0.60 log unit. Moreover, all of the deviations for σ^+-constants are negative while for σ-constants two deviations are positive (*p*-chloro, *p*-phenyl) and two are negative (*p*-*t*-butyl, *p*-methyl). The total negative deviations are 0.21 log unit while the positive deviations total 0.19 log unit. Recalculation of the best straight line using the four additional points and their σ-constants, yields the equation, log relative reactivity = $0.06 - 1.23\ \sigma$, with a standard deviation of 0.085 log unit. It thus appears that the transition state for the attack of a chlorine atom upon a benzyl hydrogen atom is best represented by I and not by II, although the need for more data, particularly in regard to *p*-alkoxytoluenes, is evident.

Similarly, the reaction of the 1-cyano-1-cyclohexyl radical with substituted thiophenols

$$R\cdot + HSC_6H_4Y \longrightarrow RH + YC_6H_4S\cdot$$

gives excellent agreement with σ-constants, even with the *p*-methoxy substituent.[11] Here structure IV (with $R = YC_6H_5S$) would be quite unstable because of the unfavorable charge separation, and the polar effect is best explained by a consideration of structure I.

Further examples of polar effects in the reactions of free radicals are furnished by the addition of radicals to olefins. A pronounced polar effect has been found in the reactions of radicals with a high electron affinity with substituted styrenes. For example, a polymer radical terminating in a maleic anhydride unit would be expected to have a high electron affinity because of the stability of the corresponding anion. It has been suggested that the reaction of a polymeric maleic anhydride radical with styrene would be expected to involve transition state stabilization similar to VI.[5]



VI

Again the importance of VI in the transition state should be a function of the σ^+-parameters of Y whereas the electron density of the double bond of styrene should more closely parallel σ-parameters. Support for VI is found in the conclusion that the relative reactivities of a number of substituted α-methylstyrenes towards polymeric maleic anhydride radicals or *S*-thioglycolic acid radicals, are better correlated by σ^+-constants than by σ-constants.[12]

SCHENECTADY, N. Y.

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(11) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Rev. trav. chim.*, **76**, 180 (1957).

(12) Pertinent data are summarized in ref. 5. For this correlation a σ^+-parameter for the *p*-dimethylamino group is necessary. From the results summarized by Deno and Evans (ref. 8c) an average value of −1.70 is indicated. Mayo and Walling (ref. 5) discuss the serious deviation of plots using σ-constants and point out that the deviations are similar to those observed in the hydrolysis of benzhydryl or triarylmethyl chlorides.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRESBYTERIAN COLLEGE]

The Rearrangement of the Stereoisomeric Camphorquinone-3-hydrazones

K. N. CARTER

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The *syn*- and *anti*-camphorquinone-3-hydrazones have been rearranged to α-camphoramic acid by means of sodium nitrite and concentrated sulfuric acid. Isomer interconversion was found to occur under the influence of concentrated sulfuric acid alone. The rearrangement results have been interpreted on the basis of *anti*-migration. A possible mechanism is suggested. The similarity of the rearrangement to the second type Beckmann is noted.

The rearrangement of hydrazones to amides

$$R_2C{=}NNH_2 \longrightarrow RCONHR$$

discovered by Pearson and Greer[1] when applied to the stereoisomeric hydrazones[2] of *p*-methoxybenzophenone and *p*-bromobenzophenone gave results which allowed structures to be assigned based on the assumption of *anti*-migration as is known to occur in the Beckmann rearrangement of oximes. The present work is a study of the rearrangement behavior of the stereoisomeric camphorquinone-3-hydrazones whose structures were already known.

The *syn*- and *anti*-isomers of camphorquinone-3-hydrazone were prepared and well characterized

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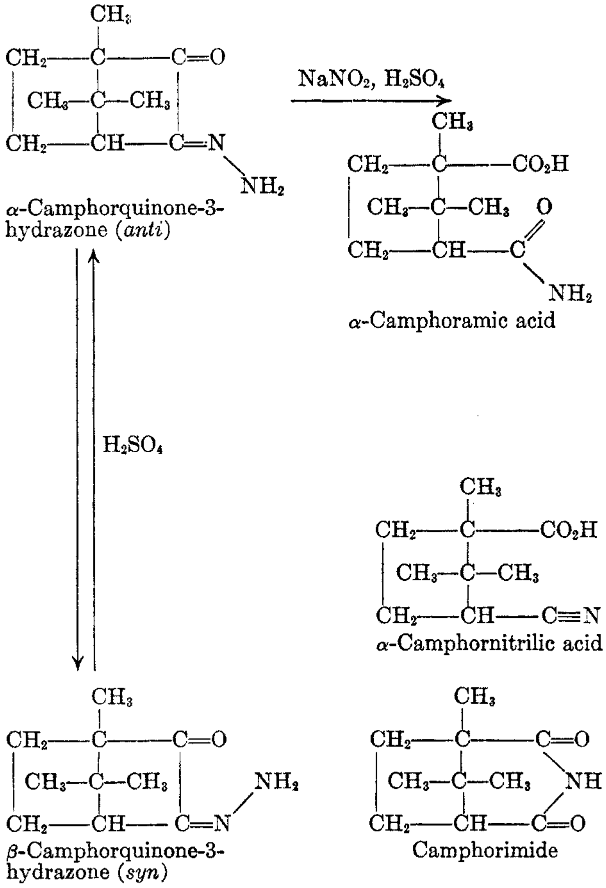
(1) D. E. Pearson and C. M. Greer, *J. Am. Chem. Soc.*, 71, 1895 (1949).

(2) D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Am. Chem. Soc.*, **75**, 5905 (1953).

by Forster and Zimmerli.[3] They also assigned configurations to the isomers by the relationship of physical properties such as melting point and solubility to those of the isomeric semicarbazones, which they also prepared and to which they were able to assign configurations because one form underwent cyclization while the other did not. The configurations of the hydrazones were reported as follows. α-Form, *anti*-configuration; β-form, *syn*-configuration. While direct chemical correlation of the hydrazones with the semicarbazones was unsuccessful, cryoscopic data[4] and the greater volatility of the β-isomer establish the structure of the hydrazones with reasonable certainty.

When subjected to the sodium nitrite–sulfuric acid rearrangement as described in the Experimental section, both isomers gave good yields of α-camphoramic acid. This suggested that one isomer changed into the other under the influence of the sulfuric acid. A study of the behavior of the isomers when treated with concentrated sulfuric acid alone showed that each isomer was converted into an equilibrium mixture of the two. Assuming *anti*-migration the course may be interpreted as follows.



Camphorimide is not postulated as an intermediate in the hydrazone rearrangement since subjection of camphorimide to rearrangement conditions gave back camphorimide in good yield, and no α-camphoramic acid was isolated.

A review of the Beckmann rearrangement of the camphorquinone oximes is vital to the present discussion. The reaction of either of the isomeric camphorquinone-2-oximes with sulfuric acid produces camphorimide[5] as does *anti*-camphorquinone-3-oxime.[6,7] Meisenheimer and Theilacker[8] found that the phosphorus pentachloride rearrangement of *anti*-camphorquinone-3-oxime gave α-camphornitrilic acid and that *syn*-camphorquinone-3-oxime under the same conditions gave α-camphornitrilic acid and α-camphoramic acid. They suggested that camphorimide might be an intermediate since Bredt and Iwanoff[9] had shown that α-camphornitrilic acid could be prepared from camphorimide and phosphorus pentachloride. Nagata and Takeda[10] have recently made a careful study of the rearrangement of *anti*-camphorquinone-3-oxime. They found that sulfuric acid produced α-camphoramic acid, α-camphornitrilic acid, and camphorimide, the relative proportions depending upon the temperature. A study on the reaction products showed that sulfuric acid with α-camphoramic acid gave camphorimide in good yield. α-Camphornitrilic acid and sulfuric acid gave camphorimide and a small amount of α-camphoramic acid. Therefore, it was concluded that the rearrangement product was α-camphornitrilic acid and that the other substances were produced from it. The phosphorus pentachloride rearrangement of *anti*-camphorquinone-3-oxime was also studied by Nagata and Takeda. They found α-camphornitrilic acid to be the product, as had Meisenheimer and Theilacker. In addition, they made a study of the reaction of phosphorus pentachloride with camphorimide and found that under rearrangement conditions no reaction occurred. The final conclusion was that the Beckmann rearrangement (second type) of *anti*-camphorquinone-3-oxime involved cleavage to nitrile without formation of an intermediate amide or imide.

It seems unlikely, then, that a cyclic intermediate is involved in either the oxime or hydrazone rearrangement. A possible mechanism for the rearrangement of α-camphorquinone-3-hydrazone may be represented as shown herewith.

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[3] M. O. Forster and A. Zimmerli, *J. Chem. Soc.*, **97**, 2156 (1910).

[4] Han-Ching Yuan and Kou-Ching Hua, *J. Chinese Chem. Soc.*, **7**, 76 (1940).

[5] J. L. Simonsen, *The Terpenes*, 2nd Ed., Cambridge University Press, Cambridge, 1949, Vol. II, p. 520.

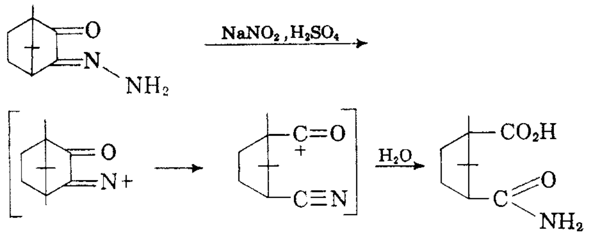
[6] A. Angeli, *Ber.*, **26**, 58 (1893).

[7] O. Manasse, *Ber.*, **26**, 241 (1893).

[8] J. Meisenheimer and W. Theilacker, *Ann.*, **493**, 33 (1932).

[9] J. Bredt and A. Iwanoff, *Ber.*, **58**, 56 (1925).

[10] W. Nagata and K. Takeda, *J. Pharm. Soc. Japan*, **72**, 1566 (1952).



The pair of electrons transferred from the C—C bond in the formation of the C≡N bond is shown as an *anti*-migration. β-Camphorquinone-3-hydrazone is assumed to change into the α-isomer before rearrangement takes place, a possibility demonstrated by the isomerization studies. At no time was any product detected that would be expected to arise from an *anti*-migration involving the β-isomer.

EXPERIMENTAL[11]

Preparation of the hydrazones. The isomeric hydrazones were prepared by the method of Forster and Zimmerli.[3] To a solution of 32.2 g. (0.194 mole) of camphorquinone, m.p. 198–199° (prepared[12] from D-camphor), in 35 ml. of hot ethanol was added 18.5 g. (0.340 mole) of 64% hydrazine solution. The reaction mixture was allowed to stand for 40 min. during which time white crystals precipitated. These were collected by filtration, washed with ethanol, and dried, wt. 7.7 g., m.p. 197–198°. The filtrate was subjected to steam distillation. The solid volatile with steam was collected by filtration and dried; wt. 6.2 g., m.p. 96–101°. The solid which remained in the distillation flask weighed 6.7 g., m.p. 194–197°. The two high melting crops were combined and recrystallized from 240 ml. of ethanol to yield 10.4 g. (29%) of α-camphorquinone-3-hydrazone, m.p. 202.5–203.5° dec. (lit.[3] m.p. 206° dec.). The low-melting crop was recrystallized from 60 ml. of 65–110° b.p. petroleum ether to yield 4.10 g. (14%) of β-camphorquinone-3-hydrazone, m.p. 101.5–103° (lit.[3] m.p. 102°).

Rearrangement of the isomeric hydrazones to α-camphoramic acid. The rearrangements were carried out in a tall 100-ml. beaker equipped with an efficient stirrer. To 30 ml. of 90% sulfuric acid contained in the beaker and cooled to 7° was added, with stirring, sodium nitrite (2.9 g., 0.042 mole). An ice bath was used to keep the temperature between 6 and 8° during addition. The temperature was allowed to rise to 10°, and powdered α-camphorquinone-3-hydrazone (3.6 g., 0.020 mole) was carefully added over a period of about 50 min. The temperature was kept between 12 and 17° during the reaction by using an ice bath for cooling when necessary. Gas was evolved during the addition. The mixture was stirred 8 min. after addition was complete and then poured into a slurry of ice and 75 ml. of concentrated ammonium hydroxide. The *p*H of the resulting solution was adjusted to 4, and the solution was subjected to continuous ether extraction for a period of about 8 hr. The ether was removed by distillation leaving 3.7 g. (93%) of tan solid, m.p. 166.5–172°. Purification by recrystallization from ethyl acetate gave 2.9 g. (73%) of pure α-camphoramic acid, m.p. 174.5–176° (lit.[8] m.p. 174°), $[\alpha]_D$, in ethanol, +23.3° (lit.[13] $[\alpha]_D$, in ethanol, +25°), neutral equivalent 199 (calcd. 199).

Treatment of β-camphorquinone-3-hydrazone in a similar manner also gave α-camphoramic acid (80% crude, 65% pure).

An attempted rearrangement run at lower temperatures (3–6°) gave camphorquinone-3,3′-azine, m.p. 216–217° (lit.[3] m.p. 218°) as the only identified product. Rearrangement at higher temperatures (20–30°) than the range regularly used was found to occur satisfactorily.

Interconversion of isomers. α-Camphorquinone-3-hydrazone (3.6 g.) was dissolved in 90% sulfuric acid at about 12° over a period of about 8 min. and the resulting solution poured into a slurry of ice and concentrated ammonium hydroxide. The product was obtained by continuous ether extraction. Infrared analysis of one run showed the product to contain a maximum of 46% of the α-isomer and 42% of the β-isomer. (The infrared spectra in chloroform solution show a characteristic absorption at 10.51 microns for the α-isomer and 10.20 microns for the β-isomer.) The most α-isomer obtained by actual separation from any run (several were made) was 53%. The most β-isomer isolated was 22% crude steam distillate, 11% pure.

β-Camphorquinone-3-hydrazone treated in a similar manner gave a maximum of 37% α-isomer and 28% β-isomer (one run determined by infrared analysis). The most α-isomer obtained by actual separation from any run (several were made) was 22%. The most β-isomer isolated was 21% crude steam distillate, 13% pure.

Camphorquinone-3,3′-azine was probably present to some extent as an impurity. It was not isolated, but crystals having its characteristic appearance were found in some fractions during separation. As previously mentioned, the azine was formed during one rearrangement run. Also, the azine is known to be formed from the hydrazone quite rapidly in more dilute sulfuric acid solution.[3]

Subjection of camphorimide to rearrangement conditions. The camphorimide, m.p. 241–242.5° (lit.[14,15] m.p. 243°, 244°), used in this experiment was prepared from D-camphoric acid by the method of Noyes.[16] To 15 ml. of 90% sulfuric acid containing 1.45 g. (0.021 mole) of sodium nitrite was added 1.81 g. (0.01 mole) of camphorimide. The addition was carried out over a 10-min. period, and stirring was continued for 20 min. longer. The temperature was maintained at 12–17° during the 30-min. period. The solution was then poured into a slurry of ice and concentrated ammonium hydroxide after which the *p*H was adjusted to about 4. The white precipitate was collected on a filter and the filtrate extracted with chloroform. The total amount of camphorimide recovered was 1.75 g. (97%), m.p. 242–243°, recrystallized from water, wt. 1.30 g. (72%), m.p. 241.5–243°.

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CLINTON, S. C.

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(11) Melting points are uncorrected. Infrared analyses were performed by Kendall Infrared Laboratories, Plainfield, N. J.

(12) W. C. Evans, J. M. Ridgion, and J. L. Simonsen, *J. Chem. Soc.*, 137 (1934).

(13) M. Delépine and M. Badoche, *Ann. chim.*, **17**, 171 (1942).

(14) W. C. Evans, *J. Chem. Soc.*, 2237 (1910).

(15) J. Bredt and K. Wornast, *Ann.*, **328**, 338 (1903).

(16) W. A. Noyes, *Am. Chem. J.*, **16**, 500 (1894).